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ABBREVIATED TITLE.	JOURNAL.
Abh. Böhm. Akad.	Abhandlungen der Böhmischen Akademie.
Abh. Deut. Naturwiss. Med. Ver. Böhmen.	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmon.
Acad. Sci. Fennicae	Acta Societatis Scientiarum Fennicae.
Agric. Bull. F. M. S.	Agricultural Bulletin of the Federated Malay States.
Agric. J. India	Agricultural Journal of India.
Agric. Ledger	Agricultural Ledger.
Agric. Res. Inst., Pusa Rep. (Bull.)	Agricultural Research Institute, Pusa, Report and Bulletins.
Allgem. Z. Bierbrau. u. Malzfabr.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Dis. Children	American Journal of Diseases of Children.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Publ. Health	American Journal of Public Health.
**Amer. J. Sci.*	American Journal of Science.
Amer. Min.	American Mineralogist.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Anal. Soc. Quim. Argentina	Anales de la Sociedad Química Argentina.
**Analyst*	Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. di Bot.	Annali di Botanica.
Ann. Chim.	Annales de Chimie.
**Ann. Chim. Analyt.*	Annales de Chimie Analytique.
Ann. Falsif.	Annales des Falsifications.
Ann. Geol. Min. Russie	Annuaire de la Géologie et de la Minéralogie de Russie.
Ann. hyg. pub. med. legale	Annales d'hygiène publique et de médicine légale.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. R. Staz. Chim. Agrar. Sperim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Ann. Soc. Geol. Belg.: Publ. rel. au Congo Belge	Annales de la Société géologique de Belgique: Publications relatives au Congo Belge.
Apoth. Zeit.	Apotheker-Zeitung.
Arb. Gebiet. Physik, Math. Chem.	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
Arch. Anat. Physiol.	Archiv für Anatomie und Physiologie.
Arch. Chem. Mikros.	Archiv Chemie und Mikroskopie.
Arch. Entw.-mech. Org.	Archiv für Entwicklungsmechanik der Organismen.
Arch. expt. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Farm. sperim. Sci. aff.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Fisiol.	Archivio di Fisiologia.
Arch. Int. Med.	The Archives of Internal Medicine.
Arch. ital. Biol.	Archives italiennes de Biologie.
Arch. Med. Pharm. milit.	Archives de Médicine et de Pharmacie militaires.
Arch. Néerland.	Archives Néerlandaises de sciences exactes et naturelles.

ABBREVIATED TITLE.	JOURNAL.
Arch. Néerland. physiol.	Archives Néerlandaises de physiologie de l'homme et des animaux.
**Arch. Pharm.*	Archiv der Pharmazie.
Arch. Sci. biol. Petrograd	Archives des Sciences biologiques, Petrograd.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arch. Suikerind. Ned. Indie	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arkiv. Kem. Min. Geol.	Arkiv. för Kemi, Mineralogi och Geologi.
**Atti R. Accad. Lincei*	Atti della Reale Accademia dei Lincei.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Ist. Veneto Sci.	Atti del Istituto Veneto di Scienze, Ettere ed Arti.
Aust. Pharm. Notes	Australian Pharmaceutical Notes and News.
Beitr. Min. Japan	Beiträge zur Mineralogie von Japan.
Berg. Hüttenm. Rundsch.	Berg- und Hüttenmannisches Rundschau.
**Ber.*	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
**Ber. Deut. pharm. Ges.*	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Ber. Oberhess. Ges. Natur. Heilkunde.	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen.
Ber. Ohara Inst. landw. Forsch.	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
Ber. Sachs. Ges. Wiss.	Berichte über die Verhandlungen der Sächsischen Gesellschaft der Wissenschaften.
Berlin. Klin. Woch.	Berliner Klinische Wochenschrift.
**Bied. Zentr.*	Biedermann's Zentralblatt für Agrikulturchemie und rationallen Landwirtschafts-Betrieb.
Biochem. Bull.	Biochemical Bulletin.
**Biochem. J.*	Biochemical Journal.
**Biochem. Zeitsch.*	Biochemische Zeitschrift.
Bd. of Trade J.	Board of Trade Journal.
Bol. Acad. Nac. Ciencias, Cordoba.	Boletín de la Academia Nacíonal des Ciencias, Cordoba.
**Boll. Chim. farm.*	Bolletino Chimico farmaceutico.
Boll. Soc. Geol. Ital.	Bolletino della Società Geologica Italiana.
Boll. Soc. Med.-Chirurg.	Bolletino della Società Medico-Chirurgica, Pavia.
Bot. Centr.	Botanisches Centralblatt.
Bot. Gaz.	Botanical Gazette.
Brass. Malt.	Brasserie et Malterie.
Brau- u. Malzind.	Brau- u. Malzindustrie.
Braunkohle	Braunkohle.
**Brennstoff-Chem.*	Brennstoff-Chemie.
Brewers' J.	Brewers' Journal.
Brit. J. Phot.	British Journal of Photography.
Brit. Med. J.	British Medical Journal.
Brit. Pat.	British Patent.
Buletinul Chim.	Buletinul Chimie.
Bul. Soc. Chim. România	Buletinul Societătei de Chimie din România.
Bul. Soc. Romane Stiin.	Buletinul Societatii Romane de Stiinte.
Bull. Acad. roy. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci. Petrograd.	Bulletin de l'Académie Impériale des Sciences de Petrograd.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.

ABBREVIATED TITLE.	JOURNAL.
ıll. Agric. Intell. . .	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases.
ıll. Assoc. Chim. Sucr. .	Bulletin de l'Association des Chimistes de Sucre et de Distillerie.
ıll. Bureau of Standards (U.S.A.).	Bulletin of the Bureau of Standards (U.S.A.).
ıll. Com. Géol. Finlande.	Bulletin de la Commission Géologique de Finlande.
ıll. Forest Exp. Stat. Meguro.	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
ıll. gén. Thérap. . .	Bulletin général de Thérapeutique médicale, chirurgicale, obstétricale.
ıll. Geol. Inst. Univ. Upsala.	Bulletin of the Geological Institution of the University of Upsala.
ıll. Geol. Soc. Amer. .	Bulletin of the Geological Society of America.
ıll. Geol. Survey, U.S.A.	Bulletin of the U.S. Geological Survey.
ıll. Geol. Survey, West Australia.	Bulletin of the Geological Survey, West Australia.
ıll. Imp. Inst. . .	Imperial Institute Bulletin.
ıll. Johns Hopkins Hospital.	Bulletin of Johns Hopkins Hospital.
ıll. School Mines and Met., Univ. Missouri .	Bulletin of the School of Mines and Metallurgy, University of Missouri.
ıll. Sci. Pharmacol. .	Bulletin des Sciences Pharmacologiques.
'ull. Soc. chim. . .	Bulletin de la Société chimique de France.
'ull. Soc. chim. Belg. .	Bulletin de la Société chimique de Belgique.
:ll. Soc. chim. biol. .	Bulletin de la Société de chimie biologique.
ll. Soc. d'Encour. . .	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
:ll. Soc. franç. Min. .	Bulletin de la Société française de Minéralogie.
ll. Soc. Franç. Phot. .	Bulletin de la Société Française de Photographie.
ll. Soc. Ind. Mulhouse .	Bulletin de la Société Industrielle de Mulhouse.
.ll. Soc. Ind. Nord . .	Bulletin de la Société Industrielle du Nord de la France.
:ll. Soc. Oural. Sci. Nat.	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
ll. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
ll. Wellcome Trop. Res. Lab.	Bulletin of the Wellcome Tropical Research Laboratory.
iro Sci. J. . . .	Cairo Scientific Journal.
nada Dept. Mines Publ. .	Canada Department of Mines Publications.
znadian Chem. J. . .	Canadian Chemical Journal.
nadian Med. Assoc. J. .	Canadian Medical Association Journal.
outchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
ntr. Bakt. Par. . .	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
ıtr. Min. . . .	Centralblatt für Mineralogie, Geologie und Palaeontologie.
ıtr. Zuckerind. . .	Centralblatt für Zuckerindustrie.
. of Comm. J. . .	Chamber of Commerce Journal.
m. App. . . .	Chemische Apparatur.
em. Erde . . .	Chemie der Erde.
em. Ind. . . .	Chemische Industrie.
hem. and Met. Eng. .	Chemical and Metallurgical Engineering.
hem. News . . .	Chemical News.
em. Trade J. . . .	Chemical Trade Journal.
em. Umschau Fett-Ind.	Chemische Umschau über die Fett- und Harz-Industrie.
iem. Weekblad . .	Chemisch Weekblad.
iem.-Zeit. . . .	Chemiker-Zeitung.

ABBREVIATED TITLE.	JOURNAL.
Chem. Zeitsch.	Chemische Zeitschrift.
**Chem. Zentr.*	Chemisches Zentralblatt.
Chem. and Drug.	Chemist and Druggist.
Chemik Polski	Chemik Polski.
**Chim. et Ind.*	Chimie et Industrie.
Collegium	Collegium.
**Compt. rend.*	Comptes rendus hebdomadaires des Séances de l'A démie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Soci de Biologie.
Comptes rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux de Laboratoire de Car berg.
D. R.-P.	Deutsches Reichs-Patent.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulleti
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Econ. Geol.	Economic Geology.
Econ. Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Societ
Elektrochem. Zeits.	Elektrochemische Zeitschrift.
Engineering	Engineering.
Eng. and Min. J.	Engineering and Mining Journal.
Exper. Stat. Rec.	Experimental Station Record.
Farber-Zeit.	Färber-Zeitung.
Farben-Zeit.	Farben-Zeitung.
Feuerungstechnik	Feuerungstechnik.
Flora	Flora.
Földtani Közlony	Földtani Közlöny.
Fr. Pat.	French Patent.
Gas J.	Gas Journal.
Gas World	Gas World.
**Gazzetta*	Gazzetta chimica italiana.
Geol. För. Förh.	Geologiska Föreningens i Stockholm Förhandlingar
Geol. Mag.	Geological Magazine.
Gerber	Gerber.
**Giorn. Chim. Ind. Appl.*	Giornale di Chimica Industriale ed Applicata.
Gummi-Zeit.	Gummi-Zeitung.
Handl. Vijft. Nat.	Handelingen van het Vijftende Natuur.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins
Heart	Heart.
Helv. Chim. Acta	Helvetica Chimica Acta.
Hyg. Rundsch.	Hygienische Rundschau.
Indian J. Med. Res	Indian Journal of Medical Research.
India-rubber J.	India-rubber Journal.
Int. Sugar J.	International Sugar Journal.
Int. Zeitsch. phys.-chem. Biol.	Internationale Zeitschrift für physikalisch-chemis Biologie.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholars Memoirs.
Jahrb. Geol. Reichsanst.	Jahrbuch der geologischen Reichsanstalt.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Pa ontologie, Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.
Jahresber. Ges. vaterl. Kultur.	Jahresbericht der schlesischen Gesellschaft für va ländische Kultur.

ABBREVIATED TITLE.	JOURNAL.
rnk. Ann.	Jern-kontorets Annaler.
r. Agric. Res.	Journal of Agricultural Research.
r. Agric. Sci.	Journal of Agricultural Science.
Amer. Ceram. Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
Amer. Med. Assoc.	Journal of the American Medical Association.
Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
. Biol. Chem.	Journal of Biological Chemistry, New York.
Board Agric.	Journal of the Board of Agriculture.
Canad. Min. Inst.	Journal of the Canadian Mining Institute.
Chem. Ind. Tokyo	*See* Kōgyō-Kwagaku-Zasshi.
Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
Chim. physique	Journal de Chimie physique.
Coll. Agric. Tohoku	Journal of the College of Agriculture, Tohoku Imperial University, Japan.
Coll. Agric. Tokyo	Journal of the College of Agriculture, Tokyo Imperial University, Japan.
Coll. Eng. Univ. Tokyo	Journal of the College of Engineering, University of Tokyo.
. Coll. Sci. Tokyo	Journal of the College of Science, Imperial University of Tokyo.
Exp. Med.	Journal of Experimental Medicine.
. Franklin Inst.	Journal of the Franklin Institute.
Gasbeleucht.	Journal für Gasbeleuchtung und Wasserversorgung.
gen. Physiol.	Journal of general Physiology.
Genetics	Journal of Genetics.
Geol.	Journal of Geology.
Geol. Soc. Tokyo	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
Hygiene	Journal of Hygiene.
Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
Ind. Inst. Sci.	Journal of the Indian Institute of Science.
Inst. Brewing	Journal of the Institute of Brewing.
Inst. Petroleum Tech.	Journal of the Institute of Petroleum Technologists.
Landw.	Journal für Landwirtschaft.
Marine Biol. Assoc. U.K.	Journal of the Marine Biological Association of the United Kingdom.
Med. Res.	Journal of Medical Research.
Path. Bact.	Journal of Pathology and Bacteriology.
Opt. Soc. Amer.	Journal of the Optical Society of America.
Pharm. Chim.	Journal de Pharmacie et de Chimie.
Pharm. Expt. Ther.	Journal of Pharmacology and Experimental Therapeutics.
Physical Chem.	Journal of Physical Chemistry.
Physiol.	Journal of Physiology.
Physiol. Path. gén.	Journal de Physiologie et de Pathologie générale.
pr. Chem.	Journal für praktische Chemie.
Proc. Asiatic Soc. Bengal.	Journal and Proceedings of the Asiatic Society of Bengal.
Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
Roy. Army Med. Corps	Journal of the Royal Army Medical Corps.
Roy. Hort. Soc.	Journal of the Royal Horticultural Society.
Roy. Soc. New South Wales.	Journal and Proceedings of the Royal Society of New South Wales.
Roy. Soc. West Australia	Journal of the Royal Society of West Australia.

ABBREVIATED TITLE.	JOURNAL.
**J. Russ. Phys. Chem. Soc.*	Journal of the Physical and Chemical Society o Russia.
J. Scot. Met. Soc.	Journal of the Scottish Meteorological Society.
J. Soc. Arts	Journal of the Royal Society of Arts.
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Soc. Leather Trades Chem.	Journal of the Society of Leather Trades Chemists.
J. Soc. Glass Technology	Journal of the Society of Glass Technology.
J. S. African Assoc. Anal. Chem.	Journal of the South African Association of Analytica Chemists.
J. Textile Inst.	Journal of the Textile Institute.
J. Usines Gaz	Journal des Usines à Gaz.
J. Washington Acad. Sci.	Journal of the Washington Academy of Science.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Stee Institute.
K. Svenska Vet.-Akad. Handl. *	Kongliga Svenska Vetenskaps Akademiens Hand lingar.
Kentucky Exp. Stat. Bull.	Kentucky Experimental Station, Bulletin.
Keram. Rundsch.	Keramisch Rundschau.
Kew Bull.	Kew Bulletin.
Kongl. Landtbr. Handl. Tidskr.	*See* Bull. Agric. Intell.
Kōgyō-Kwagaku-Zasshi (J. Chem. Ind. Japan).	Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry Japan).
**Kolloid Zeitsch.*	Kolloid Zeitschrift.
**Koll. Chem. Beihefte*	Kolloid-chemische Beihefte.
Kosmos	Kosmos (Lemberg).
Kühn-Archiv	Kühn-Archiv.
Kunststoffe	Kunststoffe.
Lancet	The Lancet.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs.-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Leather Trades Rev.	Leather Trades Review.
Le Radium	Le Radium.
Local Govt. Bd. Reports	Local Government Board Reports.
Louisiana Bull.	Louisiana Bulletin.
Louisiana Planter	Louisiana Planter.
Lunds. Univ. Arsskr.	Lunds Universitets Års-skrift.
Math. és Termés. Ért.	Mathematikai és Természettudományi Értesitö, Buda pest.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetonskapsakademiens Nobel Institut.
Medd. om Grönland	Meddelser om Grönland.
Med. Chron.	Medical Chronicle.
Med. Klinik	Medizinesche Klinik.
Mem. Acad. Sci. Petrograd.	Mémoires de l'Académie Impériale des Sciences de Petrograd.
Mem. Accad. Lincei	Memorie della Reale Accademia dei Lincei.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze d Torino.
Mem. Coll. Sci. Kyōtō	Memoirs of the College of Science, Kyōtō Imperia University.
Mem. Coll. Sci. and Eng. Kyōtō Imp. Univ.	Memoirs of the College of Science and Engineering Kyōtō Imperial University.
Mem. Dept. Agric. India	Momoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literar and Philosophical Society.
Mem. Soc. Ing. Civ.	Mémoires de la Société des Ingénieurs Civils de France.
Mem. Soc. Natur. Kiev	Mémoires de la Société des Naturalistes de Kiev.

ABBREVIATED TITLE.	JOURNAL.
Mem. Soc. Toscana Sci. Nat.	Memorie della Società Toscana di Scienze naturali residente in Pisa.
Metall u. Erz	Metall und Erz.
Metrop. Water Bd. Rep.	Metropolitan Water Board Reports.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Mitt. geol. Landesanst.	Mittheilungen der geologischen Landesanstalt von Elsass-Lothringen.
Mitt. Inst. Kohlenv.	Mitteilungen des Institutes für Kohlenvergasung und Nebenproduktergewinnung.
Mitt. k. Materialprüf.	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. med. Ges. Tokyo	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Naturforsch. Ges. Halle.	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
**Monatsh.*	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Monatsh. Math. Physik	Monatshefte für Mathematik und Physik.
**Mon. Sci.*	Moniteur Scientifique.
Month. Not. Roy. Astr. Soc.	Monthly Notices of the Royal Astronomical Society, London.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen.	Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen.
Nature	Nature.
Naturwiss.	Die Naturwissenschaften.
Naturw. Rdsch.	Naturwissenschaftliche Rundschau.
New York Agr. Expt. Sta. Bull.	New York Agricultural Experiment Station Bulletins.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
New Zealand Jnl. of Science and Technology	New Zealand Journal of Science and Technology.
Nova Acta Soc. Sci.	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nuovo Cim.	Il Nuovo Cimento.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
**Oesterr. Chem.-Zeit.*	Oesterreichische Chemiker-Zeitung.
Oil and Colour Trades J.	Oil and Colour Trades Journal.
Oil, Paint, and Drug Rep.	Oil, Paint, and Drug Reporter.
Oversigt Danske Vid. Selsk.	Oversigt over det Kongelige Danske Videnskabernes Selskab Forhandlingar.
Pahasapa Quart.	Pahasapa Quarterly.
Paper	Paper.
Papierfabr.	Papier-Fabrikant.
Perf. and Essent. Oil Rec.	Perfumery and Essential Oil Record.
Per. spis. Sofia	Periodicesko spisanie Sofia.
Petroleum	Petroleum.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
**Pharm. Weekblad*	Pharmaceutisch Weekblad.
**Pharm. Zentr.-h.*	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.

Abbreviated Title.	Journal.
Philippine J. Sci. . .	Philippine Journal of Science.
Phot. J.	Photographic Journal.
Phot. Korr. . . .	Photographische Korrespondenz.
Physical Rev. . . .	Physical Review.
Physikal. Zeitsch. . .	Physikalische Zeitschrift.
Proc. Amer. Phil. Soc. .	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc. .	Proceedings of the American Physiological Society.
**Proc. Amer. Soc. Biol. Chem.*	Proceedings of the American Society of Biologica Chemists.
Proc. Amer. Soc. Civ. Eng.	Proceedings of the American Society of Civil Engi neers.
Proc. Amer. Soc. Testing Materials	Proceedings of American Society for Testing Materials
Proc. Austral. Inst. Min. Eng.	Proceedings of the Australasian Institute of Minin Engineers.
Proc. Camb. Phil. Soc. .	Proceedings of the Cambridge Philosophical Society.
Proc. Durham Phil. Soc. .	Proceedings of the Durham Philosophical Society.
Proc. Eng. Soc. W. Pa. .	Proceedings of the Engineers' Society of Westen Pennsylvania.
Proc. Inst. Civ. Eng. . .	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech. Eng. .	Proceedings of the Institution of Mechanical Engi neers.
Proc. Inst. Min. and Met. .	Proceedings of the Institution of Mining and Metal lurgy.
**Proc. K. Akad. Wetensch. Amsterdam.*	Koninklijke Akademie van Wetenschappen te Amster dam. Proceedings (English version).
Proc. Nat. Acad. Sci. .	Proceedings of the National Academy of Sciences.
Proc. Nova Scotia Inst. Sci.	Proceedings of the Nova Scotia Institute of Science.
Proc. Phil. Soc. Glasgow .	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc. . .	Proceedings of the Physical Society of London.
Proc. Physiol. Soc. . .	Proceedings of the Physiological Society.
Proc. Roy. Inst. . .	Proceedings of the Royal Institution of Great Britain
Proc. Roy. Irish Acad. .	Proceedings of the Royal Irish Academy.
**Proc. Roy. Soc.* . . .	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin. . .	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med. . .	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania .	Proceedings of the Royal Society of Tasmania.
Proc. Soc. Exp. Biol. Med. .	Proceedings of the Society for Experimental Biolog and Medicine.
Proc. U.S. Nat. Mus. . .	Proceedings of the United States National Museum.
Proc. verb. Soc. Toscana Sci. Nat.	Processi verbali Società Toscana di Scienze Naturali.
Pulp and Paper Magazine .	Pulp and Paper Magazine.
Quart. J. Exp. Physiol. .	Quarterly Journal of Experimental Physiology.
Quart. J. Geol. Soc. . .	Quarterly Journal of the Geological Society.
Quart. J. Med.	Quarterly Journal of Medicine.
Radium in Biol. Heilkunde	Radium in Biologie und Heilkunde.
Rec. Australian Mus. .	Records of the Australian Museum.
Rec. trav. bot. Nécrland. .	Recueil des travaux botaniques Néerlandaises.
**Rec. trav. chim.* . .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett. .	Rendiconti dell' Istituto Lombardo di Scienze e Lettere.
Rend. Soc. Chim. Ital. .	Rendiconto della Società Chimica Italiana.
Rep. Aust. Assoc. Sci. .	Report of the Australian Association for the Advancement of Science.

Abbreviated Title.	Journal.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science.
Rev. gén. Bot.	Revue générale de Botanique.
Rev. Gén. Mat. Col.	Revue Générale des Matières Colorantes.
Rev. Mét.	Revue de Métallurgie.
Rev. Real Acad. Ciencias exact. Madrid.	Revista de la Real Academia de Ciencias exactas, Fisicas y Naturales de Madrid.
Riv. Min. Crist. Ital.	Rivista di Mineralogia e Cristallografia Italiana.
Sbornik Klubu Pri.	Sbornik Klubu Prirodovedeckeho (Prague).
Schweiz. Apoth. Zeit.	*Schweizerische Apotheker Zeitung.*
Schweiz. Chem. Zeit.	Schweizerische Chemiker Zeitung.
Science	Science.
Scient. Amer.	Scientific American.
**Sci. Ind. Rep. Roure-Bertrand Fils.*	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Tohoku Imp. Univ.	Science Reports, Tohoku Imperial University.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Seifenfabr.	Der Seifenfabrikant.
Seifensied. Zeit.	*Seifensieder Zeitung.*
Sitzungsber. Akad. München.	Sitzungsberichte der bayerischen Akademie der Wissenschaften zu München.
Sitzungsber. Akad. Wiss. Wien.	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. Ges. Naturwiss. Marburg.	*Sitzungsberichte der Gesellschaft zur Beförderung der* gesammten Naturwissenschaften in Marburg.
Sitzungsber. Heidelberger Akad. Wis.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Med. Naturwiss. Ges. Münster.	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen *Gesellschaft zu Münster-in-Westfalens.*
Sitzungsber. Naturforsch. Ges. Petrograd.	Sitzungsberichte der Naturforschenden Gesellschaft zu Petrograd.
Sitzungsber. Naturforsch. Ges. Rostock.	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
Sitzungsber. phys. med. Ges. Erlangen.	*Sitzungsberichte der physikalisch-medizinischen Gesellschaft* zu Erlangen.
Sitzungsber. Preuss. Akad. Wiss. Berlin.	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Arch. Physiol.	Skandinavisches Archiv für Physiologie.
Smithsonian Miscell. Coll.	*Smithsonian Miscellaneous Collections.*
**Soil Sci.*	Soil Science.
South African J. Sci.	South African Journal of Science.
Sprechsaal	Sprechsaal.
Stahl u. Eisen	Stahl und Eisen.
Staz. sper. agr. ital.	*Stazioni sperimentali agrarie italiane.*
Strahlenther.	Strahlentherapie.
Suom. Tied. Toim.	Suomalaisen Tiedeakatemian Toimituskia.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
T.	Transactions of the Chemical Society.
Tekn. Tidsk.	Teknisk Tidskrift.
Ther. Gegenw.	Die Therapie der Gegenwart.
Ther. Monatsh.	Therapeutische Monatshefte.
Times Eng. Supplt.	Times Engineering Supplement.
Tonind.-Zeit.	Tonindustrie-Zeitung.
Trans. Amer. Electrochem. Soc.	*Transactions* of the American Electrochemical Society.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals	Transactions of the American Institution of Metals.

ABBREVIATED TITLE.	JOURNAL.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Ceram. Soc. . .	Transactions of the English Ceramic Society.
**Trans. Faraday Soc.* .	Transactions of the Faraday Society.
Trans. Inst. Metals . .	Transactions of the Institute of Metals.
Trans. Iron and Steel Inst.	Transactions of the Iron and Steel Institute.
Tr. N. Eng. Inst. Min. and Met.	Transactions of the North of England Institute of Mining and Metallurgy.
Trans. New Zealand Inst. .	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc. . .	Transactions of the Pathological Society.
Trans. Roy. Irish Acad. .	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada .	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin. .	Transactions of the Royal Society of Edinburgh.
Trav. Mus. Geol. Acad. Sci. Petrograd.	Travaux de Musée Geologique près l'Academie Impériale des Sciences de Petrograd.
Trav. Soc Natur. Petrograd .	Travaux de la Société Impériale des Naturalistes de Petrograd.
Tsch. Min. Mitt. . .	Tschermak's Mineralogische Mitteilungen.
U.S. Bureau of Mines, Bull. and Tech. Papers.	United States Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau Plant Ind. .	United States Bureau of Plant Industry.
U.S. Comm. Rept. . .	United States Commerce Reports, Daily Consular and Trade Reports.
U.S. Dept. Agric. Bull. .	United States Department of Agriculture Bulletins.
U.S. Hyg. Labor. Bull. .	United States Hygienic Laboratory Bulletins.
U.S. Pat.	United States Patent.
Univ. Illinois Bull. . .	University of Illinois Bulletins.
Utah Agric. Coll. Exper. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Verh. Geol. Reichsanst. Wien.	Verhandlungen der geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze.	Verhandlungen der Gesellschaft deutscher Naturforscher und Aertze.
Verh. Naturhist. med. Ver. Heidelberg.	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
Verh. Naturhist. Rheinl. .	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
Verh. Physiol. Ges. Berlin .	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
Verh. Schweiz. Nat. Ges. .	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
Vict. Mem. Mus. Geol. Survey, Canada.	Victoria Memorial Museum Geological Survey of Canada, Bulletin.
Videnskab. Skrifter . .	Skrifter udgivne af Videnskabsselskabet i Kristiania.
Wiener Klin. Woch. . .	Wiener Klinische Wochenschrift.
Wiss. Abhandl. Physikal-Tech. Reichsanst.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Wochbl. Papierfabr. . .	Wochenblatt für Papierfabrikation.
Woch. f. Brau. . . .	Wochenschrift für Brauerei.
Zeitsch. allg. Physiol. .	Zeitschrift für allgemeine Physiologie.
**Zeitsch. anal. Chem.* . .	Zeitschrift für analytische Chemie.
**Zeitsch angew. Chem.* .	Zeitschrift für angewandte Chemie.
**Zeitsch. anorg. Chem.* .	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Biol. . . .	Zeitschrift für Biologie.
Zeitsch. deut. Geol. Ges. .	Zeitschrift der deutschen Geologischen Gesellschaft.
**Zeitsch. Elektrochem.* .	Zeitschrift für Elektrochemie.
Zeitsch. exp. Path. Ther. .	Zeitschrift für experimentelle Pathologie und Therapie.

ABBREVIATED TITLE.	JOURNAL.
Z. ges. Brauw. . . .	Zeitschrift für das gesammte Brauwesen.
Zeitsch. ges. exp. Med. .	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
Zeitsch. Hyg. . . .	Zeitschrift für Hygiene und Infektionskrankheiten.
Zeitsch. Immunit. . .	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
Zeitsch. Instrument. . .	Zeitschrift für Instrumentenkunde.
Zeitsch. Kryst. Min. . .	Zeitschrift für Krystallographie und Mineralogie.
Z. öffentl. Chem. . .	Zeitschrift für öffentliche Chemie.
**Zeitsch. physikal. Chem.* .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre.
Zeitsch. physikal. Chem. Unterr.	Zeitschrift für den physikalischen und Chemischen Unterricht.
Zeitsch. physiol. Chem. .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. prakt. Geol. . .	Zeitschrift für praktische Geologie.
**Zeitsch. Sauerstoff Stickstoff Ind.*	Zeitschrift für Sauerstoff und Stickstoff Industrie.
Z. Spiritusind. . . .	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm. .	Zeitschrift fur Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Mikrosk. .	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
**Zeitsch. wiss. Photochem.* .	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
**Zeitsch. Zuckerind. Cechoslov.*	Zeitschrift für Zuckerindustrie der Čechoslovakischen Republik.

ERRATA.

Vol. CXII (Abstr., 1917).

ge	Line	
277	4	*for* "**3 : 6-dimethyl-1 : 4-benzopyrone**" *read* "**3 : 6-dimethyl-2 : 3-dihydro-1 : 4-benzopyrone.**"
,	13	for "3 : 6-*dimethyl*-1 : 4-*benzopyrone*" read "3 : 6-*dimethyl*-2 : 3-*dihydro*-1 : 4-*benzopyrone.*"

Vol. CXIV (Abstr., 1918).

366	20	*for* "tetradimite" *read* "tetradymite."
,,	,,	,, "grunlingite" *read* "grünlingite."

Vol. CXVI (Abstr., 1919).

337	14*	for "*Aktiebolsg*" read "*Aktiebolag.*"
563	28*	col. ii. *insert* "**Jackson,** *Leonard C.*, mathematical investigation of the stability of A. W. Stewart's atom, ii, 405."

Vol. CXVIII (Abstr., 1920).

ge	Line	
75	13, 14	*for* "**Chelidoneum**" *read* "**Chelidonium.**"
131	18*, 5*	,, "**Heterotropic**" *read* "**Heterotrophic.**"
131	24*	,, "L. E. Sando" *read* "C. E. Sando."
159	17*	,, "Eisner" *read* "Elsner."
207	1	,, "**Potassium**" *read* "**Calcium.**"
,,	3	,, "Potassium" *read* "Calcium."
389	5*	,, "Zeiler" *read* "Zeller."
391	8	,, "Castaldi" *read* "Gastaldi."
438	5	,, "3-p-*hydroxy*-m-*methoxymeconine*" read "3-p-*hydroxy*-m-*methoxyphenylmeconine.*"
561	7	,, "5 : 7-*dimethoxyacetyl*-3-*methoxycoumarin*" read "5 : 7-*dimethoxyacetoxy*-3-*methoxycoumarin.*"
659	11*	,, "Capelli" *read* "Cappelli."
726	5	,, "$OMe.C_6H_4.CH.CH_2.OMe$" *read* "$OMe.C_6H_4.CH_2.CH_2.OMe$."
199	3*	,, "Heldt" *read* "Hildt."
237	15	,, "**26**" *read* "**12.**"
298	10	,, "**Rusting**" *read* "**Roasting.**"
308	5*	,, "$3H_2PO_4$" *read* "$3H_3PO_4$."
441	23	,, "**Ütö**" *read* "**Utö.**"
,,	,,	,, "*Foren.*" read "*Fören.*"
,,	25	,, "$p > v$" read "$\rho > v$."
,,	27	,, "33·54" *read* "33·64."
,,	,,	,, "104·27" *read* "104·37."
503	11*	,, "Contact with hydrogen, owing to surface combustion, raises the temperature of one helix," *read* "Contact with hydrogen, owing to the change in thermal conductivity of the gas, lowers the temperature of one helix."
729	23*	,, "Reichenstein" *read* "Reichinstein."
753	20	,, "Garner, and Dorothy Webster" *read* "Garner, Frederick Challenger, and Dorothy Webster."

* From bottom.

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

The object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. *It must be understood that as the abstracts are prepared* for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.
2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.
3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.
4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.
5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.
6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.
7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.
8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.
9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

10. Employ names such as *sodium chloride, potassium sulphate* fc inorganic compounds, and use the terminals *ous* and *ic* only in di tinguishing compounds of different orders derived from the sam elementary radicle; such, for instance, as mercurous and mercuri chlorides, sulphurous and sulphuric acids.

11. Term compounds of metallic radicles with the OH-grou *hydroxides* and not hydrates, the name hydrate being reserved for con pounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to th displaceable hydrogen of the acid, *normal* and not neutral salts, an assign names such as sodium hydrogen sulphate, disodium hydroge phosphate, &c., to the acid salts. Basic salts as a rule are best desig nated merely by their *formulae*.

13. Names in common use for oxides should be employed, fc example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphori oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

14. In open chain compounds, Greek letters must be used to indicat the position of a substituent, the letter α being assigned to the firs carbon atom in the formula, except in the case of CN and CO_2H for example, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2I$ α-iodobutane, $CH_3\cdot CH_2\cdot CH_2\cdot$C] α-cyanopropane.

15. Isomeric open chain compounds are most conveniently repr sented as substitution derivatives of the longest carbon chain in th formula; for example,

$$\begin{matrix}CH_3\\CH_3\cdot CH_2\end{matrix}\!\!>CH\cdot CH<\!\!\begin{matrix}CH_3\\CH_3\end{matrix} \text{ or } CH_3\cdot CH_2\cdot CHMe\cdot CHMe\cdot CH_3$$

should be termed $\beta\gamma$-dimethylpentane not methylethyl*iso*propy methane, and $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH\cdot CH<\!\!\begin{matrix}CH_3\\CO_2H\end{matrix}$ or $CH_3\cdot CHMe\cdot CHMe\cdot CO_2$] should be termed $\alpha\beta$-dimethylbutyric acid, not $\alpha\beta\beta$-trimethylpropioni or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

16. Use names such as methane, ethane, &c., for the norma paraffins or hydrocarbons of the C_nH_{2n+2} series of the for $CH_3\cdot[CH_2]_5\cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethyle and acetylene respectively (not ethene and ethine). Homologues (the ethylene series are to be indicated by the suffix *-ene*, and those (the acetylene series, wherever possible, by *-inene*. Adopt the nam allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

17. Distinguish all hydroxyl derivatives of hydrocarbons by name ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, c n-hydric, according to the number of OH-groups. Compounds whic are not alcohols, but for which names ending in *ol* have been use are to be represented by names ending in *ole*, if a systematic nam cannot be given, thus anisole not anisol, indole not indol. Compound such as MeONa, EtONa, &c., should be termed sodium methoxid sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to b

iven in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, mino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing he OH-group should be termed *hydroxy*-derivatives, and not oxy-derivaives; for example, hydroxyacetic and not oxyacetic acid. Compounds ontaining the analogous groups OEt, OPh, OAc, &c., should in like nanner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus -ethoxypropionic acid, $OEt\cdot CHMe\cdot CO_2H$, instead of ethyl-lactic acid; :4-diethoxybenzoic acid, $(OEt)_2C_6H_3\cdot CO_2H$, instead of diethylprotoatechuic acid; and α-acetoxypropionic acid, $OAc\cdot CHMe\cdot CO_2H$, instead f acetyl-lactic acid. Terms such as diethylprotocatechuic acid should e understood to mean a compound formed by the displacement of ydrogen atoms in the hydrocarbon radicle of protocatechuic acid by thyl, thus, $C_6HEt_2(OH)_2\cdot CO_2H$, and not $C_6H_3(OEt)_2\cdot CO_2H$, just as ibromoprotocatechuic acid is understood to be the name of a compound f the formula $C_6HBr_2(OH)_2\cdot CO_2H$.

20. The term *ether* should be restricted to the oxides of hydroarbon radicles and their derivatives, and the esters (so-called comound ethers or ethereal salts) should be represented hy names similar o those given to metallic salts.

21. When a substituent is one of the groups NH_2, NHR, NR_2, NH or IR, its name should end in *ino*; for example, β-aminopropionic acid, $IH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, β-anilino-acrylic acid, $NHPh\cdot CH{:}CH\cdot CO_2H$, -iminopropionic acid, $NH{:}CMe\cdot CO_2H$.

22. Compounds of the radicle SO_3H should, whenever possible, be ermed sulphonic acids, or failing this, sulpho-compounds; for example, enzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names nding in *ine*, as aniline instead of anilin, the termination *in* being estricted to certain neutral compounds, viz., glycerides, glucosides, itter principles, and proteins, such as palmitin, amygdalin, albumin. he compounds of basic substances with hydrogen chloride, bromide r iodide should always receive names ending in *ide* and not *ate*, as orphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 4th decade (1903–1912) should be adopted s the standard of reference on questions of nomenclature not provided r in the preceding sections.

Notation.

25. In empirical formulae the elements are to be given in the der C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the underanding of the results; as a rule, they should not be written on a parate line, but should "run on" with the text.

27. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That *formulae should be shortened* by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^α for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^β for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$.

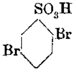
(c) That formulae should be written *in one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

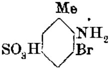
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—

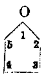


is 2 : 5-dibromobenzenesulphonic acid ;

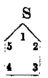


is 3-bromo-*o*-toluidine-5 sulphonic acid.

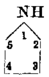
29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulae should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) should be used, of which the following schemes may be regarded as typical :—



Furan.

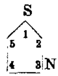


Thiophen.

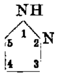


Pyrrole.

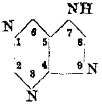
Oxazole.

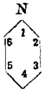


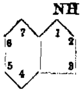
Thiazole.

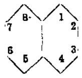


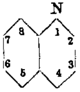
Pyrazole.

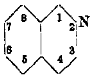

Purine.*

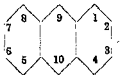

Pyridine.


Indole.


Naphthalene.


Quinoline.


*iso*Quinoline.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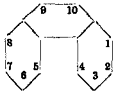
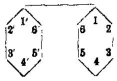
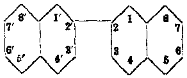

Phenanthrene.


Diphenyl


ββ-Dinaphthyl.

Manuscript.

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

Proofs.

34. Abstractors are expected to read and correct proofs carefully, and to check all formulae and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

***** The Editor's decision, in all matters connected with the Abstracts, must be considered final.**

* This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon*.

JOURNAL
OF
THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Thermal Expansion of [Solid] Paraffin and Solutions of [Solid] Paraffin. W. von Piotrowski (*Zeitsch. physikal. Chem.*, 1919, **93**, 596—606).—The specific gravity of nine specimens of solid paraffin, from naphtha, with varying points of solidification (50·5—64·0°), has been determined at temperatures between 18° and 67°, and the results compared with those found by Ziętkowski for the paraffin obtained from lignite tar (*Diss.*, Freiberg, 1900). It is found that the coefficient of expansion of solid naphtha paraffin lies between 0·000842 and 0·005108. Lignite paraffin when melted has a coefficient of expansion about twice as large as that of naphtha paraffin, but for the two solids the values are about the same. The dependence of the specific gravity of solutions on the temperature in the case of solvents of high specific gravity may be expressed by an equation based on the mixture law. In the case of solvents of low specific gravity, irregularities are found in the neighbourhood of the melting point. The specific gravity of solutions at temperatures above the melting point of the paraffin may be approximately calculated by the mixture law. J. F. S.

Low Temperature Carbonisation. Tern (*Ber.*, 1919, **52**, [*B*], 1836).—The principles of the process described by Fischer and Gluud (A., 1919, i, 377) were first applied by the author on the factory scale in 1910. J. C. W.

αγδ-Tribromopentane from αε-Dibromopentane. JULIUS VON BRAUN and GEORG KIRSCHBAUM. (*Ber.*, 1919, **52**, [*B*] 1713—1716).—Tribromides of the type

$$CH_2Br\cdot CHBr\cdot [CH_2]_n\cdot CH_2Br$$

react with magnesium to form Grignard compounds of the formula $CH_2:CH\cdot[CH_2]_n\cdot CH_2\cdot MgBr$, which may be converted into iodides $-CH_2I$, by means of iodoacetonitrile (see A., 1912, i, 434). From the magnesium compound or the iodide it would be possible to synthesise substances containing unsaturated alkyl groups, and consequently the authors have sought for methods whereby the tribromides of the desired type might be prepared conveniently, and have found the most promising material to be the αω-dibromoparaffins. These only react with bromine in the presence of iron wire, and then the reaction is vigorous and so much bromine is lost that the process must be repeated. The position of the bromine atoms in the product is not what might be expected. In the case of αε-dibromopentane, for example, the product is *αγδ-tribromopentane*, $CH_2Br\cdot CH_2\cdot CHBr\cdot CHBr\cdot CH_3$, a stable oil with spicy odour, b. p. 120—124°/11 mm., and not the expected αδε-compound b. p. 128—132°/12 mm. (A., 1918, i, 164). Its constitution is proved by converting it into Δ^{γ}-hexenoic acid,

$$CHMe:CH\cdot CH_2\cdot CH_2\cdot CO_2H,$$

through the Grignard reaction. J. C. W.

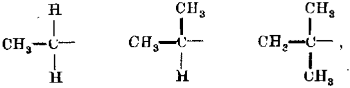
Method of Producing Methyl Alcohol from Alkyl Formates. J. A. CHRISTIANSEN (U.S. Pat. 1302011).—Methyl alcohol is produced by treating an alkyl formate with hydrogen in the presence of a catalyst, for example, partly reduced copper at 180°, $H\cdot CO_2Me+2H_2=2MeOH$. The methyl formate may be produced by leading carbon monoxide and methyl alcohol vapour at high pressure, over solid sodium methoxide, or by passing carbon monoxide into a solution of sodium methoxide in methyl alcohol, $CO+Me\cdot OH=H\cdot CO_2Me$.

The Distillation of Aqueous Solutions of Ethylene Monochlorohydrin. J. BANCELIN and G. RIVAT (*Bull. Soc. chim.*, 1919, [iv], **25**, 552—560).—The distillation of commercial aqueous solutions of ethylene monochlorohydrin gives a distillate passing at a fixed point (97·85°/760 mm.) containing 42% of the monochlorohydrin, independent of the concentration of the original solution. These results are confirmed by figures obtained with solutions made from the pure monochlorohydrin, except that in this case the distillate has a content of 41% of monochlorohydrin. Such a distillate has D^{15} 1·094. There is no direct evidence of the formation of a hydrate. W. G.

Pinacolin Transformations. V. The Varying Affinity Demands of Aliphatic Radicles. HANS MEERWEIN (*Annalen*, 1919, **419**, 121—175).—It has been shown that the pinacolin transformation is caused by the direct loss of a hydrogen atom and a hydroxyl group from the molecule of the glycol, and subsequent

migration of a radicle. With symmetrical glycols, it is a matter of indifference as to which hydroxyl group is eliminated, but with unsymmetrical glycols of the type $OH{\cdot}CR_2{\cdot}CR_2'{\cdot}OH$, two distinct products, $CR_2R'{\cdot}CO{\cdot}R'$ and $CRR_2'{\cdot}CO{\cdot}R$, result, according as the one or the other hydroxyl group is expelled. In general, the less firmly attached group will be mainly or entirely eliminated, and the nature of the pinacolin produced therefore throws considerable light on the relative strength of the attachment of the hydroxyl groups. Since, however, these may be regarded as being bound by the residue of the affinity of the carbon atom which is not required by the alkyl groups, a direct method of comparing the affinity demands of various alkyl groups is provided. A series of comparisons by this method is described in the present communication. It is found that the valency requirements of the normal alkyl groups diminish with increasing number of carbon atoms; this diminution, however, is not continuous, but exhibits a periodicity of such nature that the alkyl groups with an odd number of carbon atoms have greater affinity demands than those with an even number of carbon atoms. This apparent anomaly is, however, readily explained when the groups are formulated in the following manner, in which the light and heavy strokes represent the different affinity demands:

if, now, the *n*-propyl group is considered as formed by the displacement of a hydrogen atom in methyl by the ethyl radicle, it is seen that it must have a greater valency requirement than the ethyl group, since the demand of the latter is less than that of the methyl group. By a similar line of reasoning, it is seen that the affinity requirement must dimiuish uniformly in the case of alkyl groups with side-chains



and this appears to be the case as far as the evidence available allows conclusions to be drawn.

[With Adolf Schweinheim.]—The action of magnesium *n*-propyl bromide on methyl dimethylglycollate (compare Parry, T., 1911, **99**, 1171) leads to the formation of a mixture of *as*-dimethyldi-*n*-propylethylene glycol and dimethyl-*n*-propylethylene glycol, the Grignard compound behaving in part as a reducing agent and evolving propylene. The b. p.'s of the constituents lie so closely together that the substances cannot be separated by fractionation,

and the mixture was therefore submitted to the action of ice-cold concentrated sulphuric acid, whereby propyl *iso*propyl ketone, b. p. 135—136° (semicarbazone, m. p. 119°), and a mixture of the theoretically possible pinacolins were obtained. The latter are conveniently separated and approximately estimated by taking advantage of the great differences in the readiness with which they react with semicarbazide and the widely differing solubilities of the semicarbazones. *ααα-Methyldi-*n*-propylacetone* [*methyl α-methyl-α-propylbutyl ketone*], $CMePr_2{\cdot}COMe$, is an oil with a pronounced camphoraceous odour, b. p. 191·5—192°, D_4^{20} 0·8351, n_D^{20} 1·42927 (*semicarbazone*, coarse needles, m. p. 149—150°), whilst n-*propyl αα-dimethylbutyl ketone*, $CMe_2Pr{\cdot}COPr$, has b. p. 188·5—189°, D_4^{20} 0·8295, n_D^{20} 1·42634 (*semicarbazone*, slender needles, m. p. 104°). The ratio of the amounts of the latter to the former in the mixture is 10 : 8. A similar ratio (11 : 8) was obtained by oxidising the mixture with boiling dilute nitric acid and separating the acids formed; in this manner, αα-dimethylvaleric acid, b. p. 105—108°/14 mm., and *α-methyl-α-*n*-propylvaleric acid*, b. p. 118—122°/14 mm., m. p. 43—44°, were obtained. A mixture of *dimethylmonobutylethylene glycol* [*β-methylheptane-βγ-diol*], b. p. 109—113°/10·5 mm., and as-*dimethyldi-*n*-butylethylene glycol* [*β-methyl-γ-butylheptane-βγ-diol*], m. p. 32—32·5°, b. p. 130·5—131°/9 mm., was prepared from magnesium *n*-butyl bromide and dimethylglycollic ester; the latter glycol yielded a mixture of pinacolins, which could be separated and approximately analysed by means of semicarbazide. *Methyl-αα-di-*n*-butylacetone* [*γ-methyl-γ-butylheptane-β-one*] forms a colourless oil with a peculiar, sweet odour, b. p. 107·5—108·5°/14 mm., D_4^{20} 0·8380, n_D^{20} 1·43667 (*semicarbazone*, coarse needles, m. p. 108°), the constitution of which is deduced by its oxidation with dilute nitric acid to *α-methyl-α-*n*-butylvaleric acid*, a viscous oil, b. p. 158—159°/18 mm. n-*Butyl* tert.-*heptyl ketone* [*εε-dimethyldecane-ζ-one*] is a colourless, mobile oil, b. p. 105·5—106·5°/15 mm., D_4^{20} 0·8323, n_D^{20} 1·43420, and is transformed by nitric acid into *αα-dimethylvaleric acid*, b. p. 120—122°/15 mm. The ratio of butyl *tert.*-heptyl ketone to methyldibutylacetone in the pinacolin mixture is approximately 7 : 4.

The investigation has been extended to tetraethylethylene glycol, since, according to Kohn (A., 1905, i, 928) and Samec (A., 1907, i, 746), this substance does not yield a true pinacolin, but an isomeric alkylene oxide. This supposition is based on the facts that it does not yield an oxime and is indifferent towards zinc ethyl. It is now shown however, that the glycol actually yields ethyl *tert.*-heptyl ketone [γγ-diethylhexane-δ-one], b. p. 194—195°, D_4^{20} 0·8501, n_D^{20} 1·43519, as is shown by the formation of αα-diethylbutyric acid, m. p. 38°, b. p. 121—122°/16 mm., $D_4^{40\cdot3}$ 0·9119, $n_D^{40\cdot3}$ 1·42778 (*sodium* salt, leaflets, $+3H_2O$), when the latter is oxidised with dilute nitric acid.

The relative firmness of attachment of the methyl and ethyl groups is further demonstrated in the behaviour of *αα-diphenyl-*

β-methylethylethylene glycol [*αα-diphenyl-β-methylbutane-αβ-diol*], which is obtained as a colourless, very viscous oil, b. p. 202°/2 mm., by the action of magnesium phenyl bromide on methyl nethylethylglycollate. The glycol is transformed by concentrated ulphuric acid exclusively into *αα-diphenyl-α-ethylacetone* [*γγ-di-henylpentane-δ-one*], coarse leaflets, m. p. 27°, b. p. 179°/11 mm. *semicarbazone*, slender needles, m. p. 199—200°), the constitution f which is deduced from its conversion by sodium hypobromite nto *αα*-diphenylbutyric acid, m. p. 172—173·5°, and from its ransformation by soda-lime into *αα*-diphenylpropane, b. p. 74—280°, and acetic acid.

[With Fritz Kremers.]—As in previous cases, the action of nagnesium *n*-propyl bromide on methyl 1-*cyclo*pentanol-1-carb-xylate gave rise to a mixture of "*propyltetramethyleneglycol*" .-*α-hydroxybutyl*cyclo*pentan*-1-*ol*], $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!\!>C(OH)\cdot CHPr\cdot OH$, nd "as-*di*-n-*propyltetramethyleneglycol*" [1-*α-hydroxy-α-propyl-utyl*cyclo*pentan*-1-*ol*], $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!\!>C(OH)\cdot CPr_2\cdot OH$, which could ot be separated satisfactorily by fractional distillation, and was ierefore immediately submitted to the dehydrating action of queous oxalic or concentrated sulphuric acids, the products of hich were *butyryl*cyclo*pentane*, colourless oil, b. p. 198° (*oxime*, olourless oil, b. p. 135—138°/21 mm., *semicarbazone*, slender eedles, m. p. 110—111°), and a mixture of pinacolins, which were parated through their semicarbazones. *1:1-Dipropyl*cyclo*hexan-one* is a colourless oil with an intense odour of peppermint, b. p. 9—120°/17 mm., D_4^{20} 0·9062, n_D^{20} 1·46172 (*semicarbazone*, slender eedles grouped in rosettes or large, transparent, apparently mono-inic prisms, m. p. 182°), which is not readily oxidised by nitric id to *αα*-dipropyladipic acid; that the acid is actually formed, owever, could be shown by converting the product of oxidation to its dimethyl ester (b. p. 158—160°/18 mm.), transforming the tter into methyl dipropyl*cyclo*pentanonecarboxylate, and further to 2:2-dipropyl*cyclo*pentanone (A., 1913, i, 485), the semicarb-one of which had m. p. 211°. 1-*Butyryl*-1-*propyl*cyclo*pentane* rms a colourless, volatile oil with an odour of peppermint, b. p. .5—117°/18 mm., D_4^{20} 0·8952, n_D^{20} 1·45544 (*semicarbazone*, m. p. .6°), the constitution of which follows from its smooth oxidation · 1-*propyl*cyclo*pentane*-1-*carboxylic acid*, colourless needles, m. p. °, b. p. 142°/18 mm.

The action of magnesium ethyl bromide on methyl *cyclo*hexan-1--1-carboxylate (b. p. 96°/16 mm.) yielded a mixture of "as-*di-hylpentamethylene glycol*" [1-*α-hydroxy-α-ethylpropyl*cyclo*hexan-ol*] and "*ethylpentamethylene glycol*" [1-*α-hydroxypropyl*cyclo-*xan*-1-*ol*], which could be incompletely separated, since the latter adually crystallised in needles, m. p. 61—63°. The yield of nacolin was unusually poor, and separation of the mixture of tones was readily effected, since only the propionyl*cyclo*hexanone ormed by loss of water from the residual "ethylpentamethylene

glycol"), colourless oil with the odour of amyl acetate, b. p. 196°/atmospheric pressure, 88—89°/19 mm., D_4^{20} 0·9105, n_D^{20} 1·45304 (*semicarbazone*, shining leaflets, m. p. 150—152°), proved capable of forming an *oxime*, four-sided plates, m. p. 70—72°. The portion which did not react with hydroxylamine consisted solely of 1-*propionyl*-1-*ethyl*cyclo*hexane*, colourless oil with the odour of peppermint, b. p. 109—111°/21 mm., D_4^{20} 0·9178, n_D^{20} 1·46292, the constitution of which follows from its unusually smooth oxidation to 1-*ethyl*cyclo*hexane*-1-*carboxylic acid*, m. p. 39—40°, b. p. 140°/15 mm.

It has been shown previously (A., 1913, i, 485) that hydroxybenzhydryl*cyclo*hexanol passes by loss of water into a so-called α-pinacolin, the corresponding oxide; it has now been found possible to convert the latter into the true β-pinacolin, 1-*benzoyl*-1-*phenyl*cyclo*hexane*, prisms, m. p. 73—74°, the constitution of which is deduced from its smooth fission by fusion with potassium hydroxide into phenyl*cyclo*hexane, m. p. 7°, b. p. 235—236°, and benzoic acid.

H. W.

Catalytic Preparation by the Dry Way of Ethyl Ether. A. Mailhe and F. de Godon (*Bull. Soc. chim.*, 1919, [iv], **25**, 565—568).—Aluminium oxide, as the catalyst, was prepared by heating commercial alum to 190—195°. Using a suitable amount of catalyst, disposed in four units, and heated in each case to 190—195°, a yield of ethyl ether equivalent to 71·3% of the theory was obtained when using 95% alcohol. The yield depends rather on the weight of the catalyst employed than on the surface exposed. It is also dependent on the concentration of the alcohol used.

W. G.

Action of Methyl Alcohol on Sulphuryl Chloride and on Methyl Chlorosulphonate. R. Levaillant and L. J. Simon (*Compt. rend.*, 1919, **169**, 854—857).—The action of methyl alcohol on sulphuryl chloride may be considered as occurring in two stages, namely,

(1) $SO_2Cl_2 + MeOH = OMe{\cdot}SO_2Cl + HCl$,

(2) $OMe{\cdot}SO_2Cl + MeOH = Me_2SO_4 + HCl$.

Another reaction, more important than that represented in (2), occurs, however, $OMe{\cdot}SO_2Cl + MeOH = MeHSO_4 + MeCl$. There are other secondary reactions, such as that of the hydrogen chloride and methyl alcohol with production of methyl chloride and water, which may affect the ultimate results of all the changes. The methyl hydrogen sulphate formed according to the third equation decomposes on distillation, giving methyl sulphate and sulphuric acid. By suitably modifying the conditions, a good yield of methyl chlorosulphonate may be obtained. [See, further, *J. Soc. Chem. Ind.*, 1919, 962A.]

W. G.

Preparation and Physical Properties of Dinitroglycol [Ethylene Dinitrate]. I. and II. Annibale Moreschi (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 393—397, 428—431).—Ethylene

dinitrate has been prepared according to the scheme: ethylene ⟶ ethylene dibromide ⟶ ethylene diacetate ⟶ ethylene glycol ⟶ ethylene dinitrate, the ethylene used being obtained in 96% yield by passing alcohol vapour over alumina heated at 350—360°, and the nitration of the glycol effected by means of a mixture of sulphuric and nitric acids. The specific gravities of ethylene dinitrate at $t°/4°$ vary rectilinearly with the temperature, and between 0° and 41·5° are given by the expression

$$1{\cdot}4883[1-0{\cdot}000775(t-15)];$$

the corresponding expression for glyceryl trinitrate between 0° and 55·5° is $1{\cdot}5984[1-0{\cdot}0008577(t-15)]$. The surface tension is also a linear function of the temperature: for ethylene nitrate, $4{\cdot}76(1-0{\cdot}0021t)$, and for glyceryl trinitrate, $5{\cdot}18(1-0{\cdot}003t)$. The viscosity of glyceryl trinitrate is far greater, and below 20° increases far more rapidly with fall of temperature, than that of ethylene dinitrate. The vapour tension of ethylene dinitrate at 20° is 0·3 mm.

The properties are given of various explosive products obtained by mixing ethylene dinitrate and glyceryl trinitrate with cellulose nitrate. T. H. P.

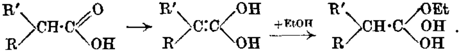
Reciprocal Influence of the Fatty Acids on the Solubility. P. WAENTIG and G. PESCHECK (*Zeitsch. physikal. Chem.*, 1919, **93**, 529—569).—The solubility of a fatty acid in certain solvents is often very much increased by the presence of a second fatty acid. The increase is always reciprocal and often very considerable. For example, the solubility of palmitic acid in carbon tetrachloride is increased 250% by the presence of lauric acid. The increase in solubility decreases with increase of the disturbing acid and approaches a limiting value. An attempt is made to explain the increased solubility by the formation of readily soluble compounds of the two acids, but a direct proof could not be obtained, for molecular weight determinations, both by the ebullioscopic and cryoscopic methods, of one fatty acid in the presence of a second gave no difference in the boiling point or freezing point from that obtained with the pure solvent. But since the fatty acids are bimolecular in the solvents in which the increase of solubility is observed, this does not disprove the absence of compounds, for such compounds could well be formed without any change occurring in the number of molecules present, thus: $L_2+P_2=2LP$. If the view is correct, the formation of compounds, and also the increase in solubility, should not take place in those solvents in which the acids are unimolecular. It is found that in carbon tetrachloride, chloroform, benzene, toluene, and nitrobenzene solutions, in which the fatty acids are bimolecular, the increase in solubility occurs, but in ethyl alcohol, ethyl ether, ethyl acetate, and benzaldehyde solutions, in which the fatty acids are unimolecular, the increase in solubility is not observed. It is also found that the increase in solubility is not restricted to the fatty acids, but occurs also with aromatic acids, and in a much smaller degree with ketones and alcohols, so that it is suggested that the subsidiary valencies of the

carbonyl oxygen are responsible for the effect. A determination of the influence of temperature on the increase of solubility indicates that temperature has practically no effect on the increase. It is also shown that temperature has no influence on the association of the fatty acids in solution. The solubility of palmitic acid is influenced by the quantity of undissolved acid, and also to a very marked extent by traces of moisture. During the purification of palmitic acid, it was found that the solubility in a stated volume of a given solvent furnished a much better criterion of the purity of the acid than did the melting point. The density and vapour tension of liquid mixtures of fatty acids were determined, and it is shown that the values are not in keeping with the mixture law, from which it is deduced that compounds of the two acids are present in the fused mass. From the fusion curve of mixtures of palmitic and lauric acids, it is shown that an equimolecular compound of the two acids exists in the solid state. J. F. S.

Preparation of Chloromethyl Chloroformates. André Kling, D. Florentin, A. Lassieur, and R. Schmutz (*Compt. rend*, 1919, **169**, 1046—1047).—Carbonyl chloride condenses with methyl alcohol to give methyl chloroformate, which when acted on by chlorine in sunlight gives chloromethyl chloroformate, then dichloromethyl chloroformate, and finally the trichloromethyl ester. It is almost impossible to separate the first two esters by fractional distillation, but the dichloro- and trichloro-derivatives can be separated in this way. An alternative method is to chlorinate methyl formate in sunlight, but in this case some dichloromethyl formate is obtained. W. G.

Anomalies in the Formation of Esters from Acids and Alcohols. E. Preiswerk (*Helv. Chim. Acta*, 1919, **2**, 647—654). —Diethylmalonic acid cannot be esterified by alcohol and sulphuric acid or hydrogen chloride, the only ester which can be isolated being ethyl α-ethylpropionate in small quantity. Under similar conditions, ethyl malonate is formed in good yield from malonic acid.

A critical review of the literature on esterification leads the author to the conclusion that it is primarily an additive process. In general, however, there is but little tendency for the carbonyl portion of the carboxyl group to form additive compounds unless it is influenced by the presence of a neighbouring carbonyl group (as in oxalic or pyruvic acids) or by the tendency towards enolisation of a hydrogen atom in the α-position:



Esterification, according to this hypothesis, should occur most readily with acids containing a mobile α-substituted hydrogen atom, and this appears to be the case when, for example, chloroacetic, cyanoacetic, and phenylacetic acids are compared with acetic

acid. As usually formulated, benzoic acid does not contain a hydrogen atom in the α-position, and yet it is readily esterified; the author seeks an explanation of the apparent anomaly in the oscillation hypothesis, which postulates the presence of the hydrogen atom *in this position during the half-interval of time.* The catalytic acceleration of esterification by mineral acids is attributed to the suppression of the ionisation of the organic acid, and consequent increase in the enolisation. H. W.

Some Ternary Systems containing Alkali Oxalates and Water. ALBERT CHERBURY DAVID RIVETT and EDMUND ARTHUR O'CONNOR (T., 1919, **115**, 1346—1354).

Preparation of Maleic Acid. JOHN M. WEISS and CHARLES R. DOWNS (U.S. Pat. 1318632).—A mixture of benzene and benzoquinone in the vapour phase is oxidised by treatment under pressure with a gas containing oxygen at a temperature of 300—700° in the presence of vanadium oxide. The maleic acid produced is separated, and the residual, unchanged benzene and benzoquinone are again subjected to the same treatment.

G. F. M.

Slow, Partial Change of an Aqueous Solution of Maleic Acid into Fumaric Acid at the Ordinary Temperature and in the Absence of Light. ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1919, **93**, 613—616).—From electro-conductivity measurements with a solution of maleic acid which had been kept in the dark for five years, it is shown that about 4% of the acid had become changed into fumaric acid. J. F. S.

Various Bismuth Compounds. L. VANINO and F. MUSSGNUG (*Arch. Pharm.*, 1919, **257**, 267—269).—The following bismuth salts have been prepared with the help of bismuth–mannitol solution, obtained by grinding together crystalline bismuth nitrate (1 mol.) and mannitol (1 mol.) and treating the mass with water.

Bismuth anhydromethylenecitrate, $Bi_2(C_7H_6O_7)_3,6H_2O$, prepared from the corresponding sodium salt ("citarine") and bismuth–mannitol, forms an odourless, white, granular powder, and is reduced to metallic bismuth when heated with alkali hydroxide.

Bismuth diethylmalonate, $Bi_2(C_7H_{10}O_4)_3$, is obtained as a voluminous, white precipitate from the sodium salt and bismuth–mannitol solution.

Bismuth mandelate, $Bi(C_8H_7O_3)_3$, prepared from mandelic acid and bismuth–mannitol solution, forms a white, indistinctly crystalline precipitate, m. p. 210—215° (decomp.).

Bismuth vanillate, $Bi(C_8H_7O_4)_3,2H_2O$, obtained from the sodium salt and bismuth–mannitol solution, forms yellowish-white, nodular crystals with no sharp melting point.

Bismuth cinnamate, $Bi(C_9H_7O_2)_3,3H_2O$, forms nodular crystals with an indistinct melting point.

Bismuth acetate may be prepared in 95% yield by heating bismuth

oxide or hydroxide in a reflux apparatus with acetic anhydride, its formation being accelerated by the presence of a little glacial acetic acid. T. H. P.

Preparation of Formaldehyde from Formates. H. and S. (*Caoutchouc et Guttapercha*, 1919, **16**, 9803; from *Chem. Zentr.*, 1919, iv, 412).—Formaldehyde is produced when metallic formates are heated, the necessary temperature increasing with increase in the basic properties of the metal. The optimum temperatures are as follows: Cu, 170°; Pb, 195—200°; Ni, 210°; Zn, 240°; Fe, 245°; Mn, 295°; Ba, 325°; Ca, 335°; Mg, 340°; Sr, 355°; Na, 355°; K, 375°. A large portion of the formaldehyde is immediately transformed into methyl alcohol and formic acid. Methyl alcohol and formaldehyde are produced when formic acid is passed at the high temperature over zinc oxide or thorium oxide. H. W.

Diastase-like Properties of Formaldehyde. Action of Formaldehyde on Starch. HARRY MAGGI (*Fermentforsch.*, 1919, **2**, 304—447; from *Chem. Zentr.*, 1919, iii, 635).—The main results obtained in the investigations have already been reported by Woker. The apparent degradation of starch appears to proceed most readily in faintly acid solution. Experiments are now recorded on the action of mixtures of formaldehyde or saliva with glycogen solution and iodine and on the precipitation of starch or glycogen by formaldehyde. The latter phenomenon is also observed with formic or other acids. A method of estimating diastase, based on the alteration in shade in the mixtures described above, could not be worked out in consequence of this action. H. W.

The Diastase-like Properties of Formaldehyde. G. WOKER and H. MAGGI (*Ber.*, 1919, **52**, [*B*], 1594—1604).—The authors reiterate their arguments in favour of the view that formaldehyde acts on starch in a certain measure like diastase, and reply to recent criticisms (A., 1919, i, 253, 311, 312). They hold the view that under the prolonged influence of formaldehyde the primary hydrolytic products are rebuilt into non-hydrolysable and non-reducing substances, such as the so-called "reversion dextrin," and in this way they meet most of the criticism, for the authors, in their desire to give the hydrolysis every assistance of time and temperature, did just the reverse by generally keeping the mixtures of starch and formaldehyde too long. A similar rebuilding of hydrolytic products is known to occur when egg albumen is digested with papain (see Abderhalden's book). J. C. W.

The Stabilisation of Acraldehyde. III. Preparation of Acraldehyde. CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1919, **169**, 885—889).—For the preparation of acraldehyde from glycerol the authors recommend the use of a mixture of 5 parts of potassium hydrogen sulphate with 1 part of potassium sulphate as a dehydrating agent. Using such a mixture, to which is added one-quarter of its weight of glycerol, the heating being

carefully controlled and the glycerol replaced as exhausted, they obtained a yield of pure acraldehyde equivalent to 67·5% of the theoretical yield. [See, further, *J. Soc. Chem. Ind.*, 1920, 42A.]

W. G.

γ-**Hydroxyaldehydes. II.** Burckhardt Helferich (*Ber.*, 1919, **52**, [*B*], 1800—1812. Compare A., 1919, i, 386).—In the former paper it was shown that γ-hydroxyvaleraldehyde behaves like a furan derivative, and yields an acetate and a methyl compound of the same type. Starting with methylheptenol, this has now been acetylated and methylated, the derivatives ozonised in glacial acetic acid, and then treated with zinc dust, giving the acetate and methyl ether of the normal form of γ-hydroxyvaleraldehyde. The isomerides differ in molecular refraction and chemical properties in the expected manner. Apparently, the free γ-hydroxyvaleraldehyde, or rather 2-hydroxy-5-methyltetrahydrofuran, is desmotropic with the true aldehyde form, thus:

$$O\Big\langle\begin{matrix}CH(OH)\cdot CH_2\\ |\\ CHMe—CH_2\end{matrix} \rightleftharpoons OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHO,$$

which may be demonstrated as follows: by adding equal quantities of Schiff's reagent or ammoniacal silver oxide to equivalent solutions of "γ-hydroxyvaleraldehyde" (1%), γ-methoxyvaleraldehyde and acetaldehyde (0·44%), the characteristic reactions are complete in a few seconds with the true aldehydes, but develop gradually with the furan derivative. Similar phenomena are exhibited by γ-hydroxyhexaldehyde.

Acetylmethylheptenol [*αε-dimethyl-Δ-hexenyl acetate*], $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot OAc$, from methylheptenol and acetic anhydride, has b. p. 78—78·5°/9 mm., $D_4^{17.9}$ 0·8928, $n_D^{17.9}$ 1·4328, and *methylheptenol methyl ether* [*β-methoxy-ζ-methyl-Δ^ε-heptene*], from methylheptenol, sodium, and methyl iodide, has b. p. 50—50·5°/9 mm., 163·5°/752 mm. (corr.), D_4^{18} 0·8103, n_D^{18} 1·4281. γ-*Acetoxyvaleraldehyde* has b. p. 88—91°/12 mm., D_4^{18} 1·011, n_4^{18} 1·4226, and is very sparingly soluble in water. γ-*Methoxyvaleraldehyde*, $OMe\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHO$, is a limpid, mobile liquid, soluble in water (1 in 5), b. p. 43—44°/10 mm., D_4^{18} 0·9161, n_D^{18} 1·4134.

Whereas the furan derivative is merely converted into its methyl ether, 2-methoxy-5-methyltetrahydrofuran, under the influence of methyl-alcoholic hydrogen chloride, the true γ-methoxyvaleraldehyde, like aldol (prepared by Grignard's method, A., 1907, i, 287), gives a dimethylacetal. *ααδ-Trimethoxypentane*, from methoxyvaleraldehyde, is a very soluble liquid with a burning taste, b. p. 72°/12 mm., D_4^{18} 0·9197, n_D^{18} 1·4119, and *αα-dimethoxybutan-γ-ol*, from aldol, has b. p. 71—76°/9 mm., D_4^{18} 0·9894, n_D^{18} 1·4200.

Just as aldol may be converted into pentan-βδ-diol by means of magnesium methyl iodide, so γ-methoxyvaleraldehyde yields *ε-methoxyhexan-β-ol*, $OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot OMe$, b. p. 79—80°/9 mm., D^{18} 0·9048, n_D^{18} 1·4263. Similarly, if the free

"γ-hydroxyvaleraldehyde" were a true aldehyde it would form th known hexane-βε-diol, but whilst it reacts to form methane, th intermediate magnesium compound regenerates the original sub stance and complex products on decomposition with dilute sulphuri acid.

Δγ-Pentenoyl chloride is slowly added to well-chilled zinc ethyl an the product is decomposed by ice, giving *ethyl Δγ-butenyl keton* $CH_2:CH\cdot CH_2\cdot CH_2\cdot COEt$, b. p. 46—47°/12 mm., $D_4^{18\cdot3}$ 0·848 $n_D^{18\cdot3}$ 1·4254, an unpleasant-smelling liquid, which forms a *semicarb azone*, thin, rhombic plates, m. p. 82—83° (corr.), and is reduce by sodium and alcohol to *Δα-hepten-ε-ol*, b. p. 60—61·5°/11 mm. D_4^{18} 0·8447, n_D^{18} 1·4369. This is ozonised as above, and thus converte into *γ-hydroxyhexaldehyde* [or, rather, the desmotrope, *5-hydrox 2-ethyltetrahydrofuran*], a fairly mobile, limpid liquid, b. p 77—80°/11 mm., D_4^{18} 1·004, n_D^{18} 1·4398, which condenses with meth alcohol to form the half-acetal, that is, *5-methoxy-2-ethyltetrahydr furan*, b. p. 139—145°/760 mm. (corr.), D_4^{18} 0·9225, n_D^{18} 1·4164, mobile oil with odour reminiscent of peppermint. J. C. W.

Manufacture of Acetone and Carbon Dioxide. SOCIÉT ANONYME DES ACIERIES & FORGES DE FIRMINY (Brit. Pat 134144).—Acetic acid of 90—100% strength is catalysed over man ganese peroxides prepared either by precipitation or by crushin and screening natural pyrolusite, pieces of a diameter of 5—7 mm being employed. Catalysis occurs without appreciable subsidiar reaction between wide limits of temperature, for instance, 350—450° The catalyst is packed in a cylinder and heated either externally o preferably, by mixing with 1—1½ volumes of crushed coke similarl screened, and passing an electric current through the mixture b means of two iron or aluminium electrodes. The acetone produce is separated from the carbon dioxide by condensation, and scrubbir in water-sprinkling towers. The catalyst is much more stable tha Sabatier's manganous oxide, and when the activity does decline, is only necessary to heat it in a current of air to revivify it.
G. F. M.

The Production of Methyl Ethyl Ketone from *n*-Buty Alcohol. ALBERT THEODORE KING (T., 1919, **115**, 1404—1410).

Physical Properties of Mannitol and its Aqueou Solutions. JOSEPH M. BRAHAM (*J. Amer. Chem. Soc.*, 1919, **4** 1707—1718).—The melting point, the specific rotation in aqueo solution, and the freezing-point solubility diagram of pure mannit up to 103° have been determined. The most trustworthy values the density, specific heat, and heat of combustion are indicated fro a discussion of the various values occurring in the literature. Th following physical constants are recorded: melting point, 166·05° specific rotation, $[\alpha]_E^{20} = -0·244 \pm 0·002°$, and $[\alpha]_E^{20}$ calculated = $-0·208 \pm 0·002°$; D 1·487 (room temperature), specific he C (28—100°) = 0·3271 cal./deg., and C (14—26°) = 0·315 cal./deg

heat of combustion, 4·00 cal./gram. Pure mannitol may be obtained from the commercial product by two crystallisations from aqueous alcohol. J. F. S.

Conversion of the Simple Sugars into their Enolic and Ethylene Oxide Forms. EDWARD FRANKLAND ARMSTRONG and THOMAS PERCY HILDITCH (T., 1919, **115**, 1410—1428).

Action of the Carbonates of the Alkaline Earths on Dextrose. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1919, **97**, 97—113).—When a solution of dextrose is boiled with calcium carbonate, it becomes brown, and gradually loses its dextro-rotation, which after prolonged boiling is entirely eliminated; the sugar may even become lævorotatory. The reducing power of the dextrose is also diminished, but to a much smaller extent. Distilled water previously shaken with calcium carbonate produces the same change, but the reduction in the rotation becomes constant after some time because the dissolved carbonate is neutralised by the acid formed in the reaction. It is concluded that the dextrose is changed into lævulose, and eventually into other lævorotatory or weakly dextrorotatory sugars. S. S. Z.

Synthesis of Disaccharides with Two Sulphur or Selenium Atoms. FRITZ WREDE (*Ber.*, 1919, **52**, [*B*], 1756—1761).—Acetobromoglucose reacts with potassium disulphide in alcohol to form a disulphide of the type R_2S_2, mixed with various by-products. Some of these are partly de-acetylated compounds, but they may be re-acetylated by means of acetic anhydride and the complication thus removed. To a certain extent the potassium disulphide reacts as a mixture of sulphur and monosulphide, the latter forming the octa-acetate of thio*iso*trehalose, R_2S (A., 1917, i, 540), and apparently also according to the scheme $R_2S_2 + 2K_2S = 2R{\cdot}SK + K_2S_2$. The mono- and di-sulphides can be separated by fractional crystallisation, and the acetyl groups removed by means of methyl-alcoholic ammonia. Similar selenium compounds may also be obtained.

Octa-acetyldithiodiglucose, $C_{28}H_{38}O_{18}S_2$, crystallises in stout crusts from benzene or long needles from methyl alcohol; m. p. 139°, $[\alpha]_D^{18}$ −177·7° in nitrobenzene. *Dithiodiglucose*, $C_{12}H_{22}O_{10}S_2$, is a hygroscopic, white powder, $[\alpha]_D^{18}$ −144·4° in water, which tastes sweet, and forms metallic salts, for example, the *potassium* salt, $C_{12}H_{20}O_{10}S_2K_2,2H_2O$. *Octa-acetyldiselenodiglucose* has m. p. 133°, $[\alpha]_D^{18}$ −133·8° in chloroform, and *diselenodiglucose* is a pale yellow powder, $[\alpha]_D^{18}$ −93·98° in water, which forms a *potassium* salt, $C_{12}H_{20}O_{10}Se_2K_2,2H_2O$. J. C. W.

Density of Pure Sucrose and the Contraction in Volume of its Aqueous Solutions. D. SIDERSKY (*Bull. Assoc. Chim. Sucr. Dist.*, 1919, **37**, 73—77).—From the tables of specific gravities of aqueous sucrose solutions compiled by Plato in 1900 (and adopted by the German *Normal Eichungs-Kommission*), the author has calculated the solution density of sugar at different concentrations, the solvent being assumed to occupy the same volume as in the pure

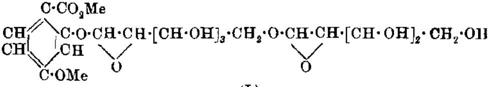
state. For concentrations ranging from 5 to 90 grams of sucrose per 100 c.c. absolute, at 15°, the solution densities range almost linearly from 1·629 to 1·591, thus approaching the density of solid sugar (1·588) as the limit of solubility is reached. The contraction which accompanies the formation of sucrose solutions increases with the concentration of sugar to a maximum value of 0·47% of the total volume for solutions containing 45—55 grams per 100 c.c., beyond which concentration it declines again, and amounts to only 0·11% for solutions containing 90 grams per 100 c.c. J. H. L.

Characteristics and Composition of Primeverose. A. Goris and Ch. Vischniac (*Compt. rend.*, 1919, **169**, 871—873).—A further study of the sugar primeverose, obtained from the two glucosides primeverin and primulaverin isolated from *Primula officinalis*, Jacq (compare A., 1913, i, 576). This sugar crystallises in the anhydrous state and has m. p. 209—210°. It shows mutarotation, initial $[\alpha]_D + 22{\cdot}70°$, final $[\alpha]_D - 3{\cdot}43°$. It reduces Fehling's solution, gives an *osazone*, m. p. 224—225°, and on hydrolysis gives one molecule of dextrose and one molecule of xylose. W. G.

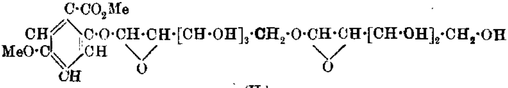
Constitution of Primeverose, Primeverin, and Primulaverin. A. Goris and Ch. Vischniac (*Compt. rend.*, 1919, **169**, 975—977).—It has previously been shown (preceding abstract) that primeverose is a biose formed by the combination of a molecule of dextrose and a molecule of xylose, and that it has a free aldehyde group. It has now been shown by controlled oxidation of the sugar and subsequent hydrolysis of the *calcium primeverobionate* formed that the free aldehyde group is in the dextrose residue. The constitution of primeverose is, therefore, given as

$$CHO\cdot[CH\cdot OH]_4\cdot CH_2\cdot O\cdot \underbrace{CH\cdot CH}_{O}\cdot[CH\cdot OH]_2\cdot CH_2\cdot OH .$$

Similarly, it has been shown that primeverin and primulaverin give, on hydrolysis, primeverose and the methyl esters of β-methoxyresorcylic acid and *m*-methoxysalicylic acid respectively. These two compounds have, therefore, the constitutions shown in formulæ I and II respectively:



(I.)



(II.)

W. G.

Systematic Ageing Experiments with Solutions of 'arious Kinds of Starch under Exact Time Conditions. 'ime Law of the Ageing of Starch Solutions. HERMANN 'ALLINGER (*Kolloid Zeitsch.*; 1919, **25**, 111—115).—Experiments on ıe ageing of starch solutions have been carried out with soluble otato starch, soluble wheat starch, soluble barley starch, and with mylodextrin from potato starch. The solutions were made up in ater, and at stated intervals 50 c.c. of the solution were treated ith 0·5 c.c. of human saliva (ptyalin) and kept for twenty-three ours at the ordinary temperature; the precipitated starch gel was ltered and dried at 110° until of constant weight. If G is the eight of gel and t the time of ageing in hours it is found that the elationship between $\log G$ and $\log t$ is represented by a straight ne, and that numerically $G=gt^a$, where g and a are constants. hese values have been determined for the starch varieties named oove, and it is shown that they are characteristic of the variety. he following values are recorded: potato starch I., $g=4·06$, $=0·445$; potato starch II, $g=3·00$, $a=0·455$; wheat starch, $=5·37$, $a=0·165$; barley starch, $g=11·17$, $a=0·214$; amylodextrin, $=3·51$, $a=0·521$. The starch solutions were aged at 7°. J. F. S.

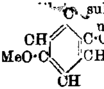
Studies in Fermentation. HERMANN SALLINGER (*Fermentforsch.*, , 449—457; from *Chem. Zentr.*, 1919, iii, 635).—A reply to Biederann (A., 1917, i, 62). The author sets out in detail the reasons hich lead him to consider the application of extremely dilute soluons, as recommended by Biedermann, unsuitable. Experiments ith sterilised starch solution failed to confirm the diastatic action saliva ash or the autolysis of starch. H. W.

Studies in Fermentation. IV. Autolysis of Starch. W. IEDERMANN (*Fermentforsch.*, **2**, 458—472; from *Chem. Zentr.*, 19, iii, 635).—The autolysis of starch might possibly be due to aces of ferments retained by the crude material. The former periments (A., 1917, i, 62; 1919, i, 107) have therefore been peated with preparations of amylose which had been purified by iling and treatment with hydrochloric acid. The experimental ocedure is very fully described. The author has endeavoured to sprove the possible criticism that the results are due to bacterial tion by control experiments in which a culture of bacteria which adily cause the fission of starch was added to the amylose solution; e achromic point was reached very much more slowly than in the esence of saliva ash or sodium chloride. The activity of the salts not due to their power of directly causing the fission of starch, it is to be ascribed to their action in facilitating the formation the ferment; when once this is attained in a sufficient degree, itolysis proceeds unaltered in a solution which has been freed from lts by dialysis. Preparations which already contain fission oducts of starch are less readily affected, and require much longer riods than pure amylose preparations. H. W.

Cellulose and Cellulose Nitrate. Absorbent Power fo Gases and Constitution. B. ODDO (*Gazzetta*, 1919, **49**, ii 127—139).—Cellulose is able to fix acid gases in definite proportio one molecule of dry hydrogen chloride being taken up per on quadrupled molecule (C_{24}) of cellulose. Of the other gases examine only ammonia is absorbed in approximately the above proportio In all cases the volumes of different gases absorbed increase wit their solubility in water and diminish in the following order: NH_3 HCl, SO_2, H_2S, N_2O, CO_2, C_2H_2, CO, O, N, CH_4, H. Charcoa which has absorbed a certain gas loses part of this when immerse in a second gas, the latter being absorbed to some extent withou chemical action taking place. A similar phenomenon sometime occurs with cellulose, but whereas carbon dioxide displaces ammoni and sulphur dioxide, it does not displace hydrogen chloride. Th latter appears, therefore, to enter into true chemical combination either being added to the ethereal oxygen with formation of a oxonium compound, $:O\!<^{H}_{Cl}$, or giving a grouping similar to tha obtained with aldehydic compounds, $\cdot CH\!:\!O + HCl = \cdot CHCl\cdot OH$.

By deca- and endeca-nitrated celluloses dry hydrogen chloride i at first absorbed with great rapidity, but after a time red vapour are emitted and, even after being kept in an evacuated space, th product contains ionic chlorine and small proportions of nitroger The volume of sulphur dioxide absorbed by nitrated cellulos (13·32% N) is about five times that absorbed by an equal weight o cellulose. T. H. P.

Nitroacetylcellulose [Cellulose Nitrate Acetate]. B. ODD (*Gazzetta*, 1919, **49**, ii, 140—145).—The author has prepared cellulose nitrate acetate by the action of boiling acetic anhydrid on a collodion cotton (11·68% N), probably consisting principall of octanitrated cellulose, $C_{24}H_{28}O_8(O\cdot NO_2)_8(OH)_4$. The percentag of nitrogen and the number of acetyl groups in the product obtaine indicate it to be a tetra-acetate octanitrate of cellulose, but cryo scopic determination of the molecular weight in acetic acid at lo concentrations (0·42—2·1%) gives results corresponding closely wit the formula $C_6H_7O_2(O\cdot NO_2)_2\cdot OAc$; as the concentration of th solution is increased, the molecular weight also increases, an reaches the quadruple value only when the concentration is abou 21%. When purified, the substance is quite white, and begins t contract at 175°, whilst at 184·5° it decomposes with evolution o gas bubbles. It does not reduce Fehling's solution, but, lik cellulose nitrate, gives a yellow coloration when moistened wit sulphuric acid and treated with a solution of iodine i n iodide. In the air it burns rapidly with an orange me, leaving a small, partly carbonised residue. It di e hot in dilute, and in the cold in concentrated, alka lution; it is soluble in concentrated sulphuric acid ercury to the solution resulting in the liberation o



T. H. P.

The Use of Thallium in Organic Chemistry. KARL FREUDENBERG and GERTRUD UTHEMANN (*Ber.*, 1919, **52**, [*B*], 1509—1513).—Thallium hydroxide or carbonate has proved useful in the isolation of acids of the gallic acid series (A., 1919, i, 413), and it is now shown that uric acid, phthalimide, and lævulose give well-defined *thallium* salts. Glycine may also be prepared from the hydrochloride of its ester by boiling this with thallium carbonate and water, filtering the precipitate of thallium chloride, saturating with hydrogen sulphide, and filtering again.

Solutions of convenient thallium compounds are prepared as follows. Thallium turnings are suspended over alcohol in an atmosphere of oxygen, when oily thallium "ethoxide" is produced, and also a 5% solution of this in alcohol. The oil is really a mixture or compound of ethoxide and hydroxide in slightly varying proportions, formed according to the equation $2Tl + O + EtOH = TlOEt + TlOH$. It is freely soluble in pure ether. The hydroxide is obtained by mixing the oil with water and evaporating the alcohol under reduced pressure. The saturated aqueous solutions are about $2N$ (400 grams per litre). A concentrated solution of a hydrogen carbonate (200 grams Tl per litre) is produced by saturating a suspension of the hydroxide with carbon dioxide.

J. C. W.

Alkylamino-chromium Compounds. IV. Compounds with Methyl-, *n*-Butyl-, and *iso*-Amyl-amines. HJ. MANDAL (*Ber.*, 1919, **52**, [*B*], 1489—1500. Compare A., 1919, i, 257).—The following *chloropentamethylaminochromic* salts have been prepared: chloride, $[CrCl(NH_2Me)_5]Cl_2$, by the action of methylamine on anhydrous chromic chloride at $-10°$ (Lang and Carson, A., 1904, i, 800); *bromide*, glistening, violet prisms, and *iodide*, by double decomposition of the chloride with the potassium haloid; *mercurichloride*, $XCl_2,3HgCl_2$, pale red, *mercuribromide*,

$$XBr_2,HgBr_2,$$

reddish-violet, stellate groups, and red *mercuri-iodide*, XI_2,HgI_2, by the addition of the potassium mercuri-haloids to the above haloids; *platinichloride*, $XPtCl_6$, microcrystalline, chamois-coloured powder, and *bismuthichloride*, $XCl_2,BiCl_3$, pale violet, by the addition of the metallic chloride to hydrochloric acid solutions of the above chloride; yellow *pentasulphide*, XS_5, by the addition of yellow ammonium sulphide to the chloride.

Chloropenta-n-*butylaminochromic chloride*,

$$[CrCl(NH_2\cdot C_4H_9)_5]Cl_2,$$

and *chloropenta*iso*amylaminochromic chloride*,

$$[CrCl(NH_2\cdot C_5H_{11})_5]Cl_2,$$

are obtained by gently boiling the amines with chromic chloride. They are successively deeper violet in colour than the lower isomerides, but they are decomposed by water and are not easy to purify.

Dichlorotetra-n-*propylaminochromic chloride*,

$$[CrCl_2(NH_2Pr^a)_4]Cl,$$

is formed as a by-product in the preparation of the pentapropyl amine compound (*loc. cit.*) if the mixture becomes too hot. It crystallises in very dark green prisms, and the *nitrate* is greyish-green. *Dichlorotetra-n-butylaminochromic chloride*, small, green prisms, and *dichlorotetraisoamylaminochromic chloride*, a greyish green powder, are prepared by the addition of concentrated hydrochloric acid to alcoholic solutions of the penta-alkylamino-compounds. J. C. W.

Manufacture of Salts or Compounds of Choline and of its Higher Homologues. VEREINIGTE CHEMISCHE WERKE (Brit. Pat., 8031 of 1914).—Solutions of the compounds or salts of choline with such acids as boric, salicylic, *o*-, *m*-, or *p*-iodobenzoic, *p*-aminophenylarsinic, 3-iodo-4-aminophenylarsinic, or formic acid, whilst having a similar action to choline itself on cell tissues when injected into the blood, have the advantage of increased stability and consequent non-formation of poisonous decomposition products. The action of these compounds is therefore quite different from that of salts of choline with mineral acids, which have a negligibly small action on living cells. [See, further, *J. Soc. Chem. Ind.*, 1920, 43A.] G. F. M.

The Decomposition of Carbamide in the Presence of Nitric Acid. TUDOR WILLIAMS PRICE (T., 1919, **115**, 1354—1360).

Compounds of Complex Cyanides with Mercuric Cyanide. D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1919, **108**, 111—112).—When a warm, concentrated aqueous solution of equivalent quantities of potassium platinocyanide and mercuric cyanide is allowed to cool, white, crystalline needles of a double salt having the composition $K_2Pt(CN)_4,Hg(CN)_2,2H_2O$ separate. A similar compound of potassium nickel cyanide and mercuric cyanide was prepared. Mercuric cyanide does not form compounds with potassium ferricyanide, cobalticyanide, chromicyanide, or with the compound $K_4Mo(CN)_8$. E. H. R.

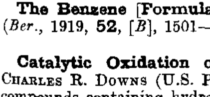
The Constitution of the Nitroprussides. I. Conductivity and Cryoscopic Measurements. GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER (T., 1919, **115**, 1429—1435).

Action of Acetylene on Arsenic Trichloride. ORVILLE A. DAFERT (*Monatsh.*, 1919, **40**, 313—323).—Acetylene does not react to any considerable extent with arsenic chloride at the ordinary temperature or at the boiling point of the latter; in the presence of anhydrous aluminium chloride at the ordinary temperature, however, *diacetylene arsenic trichloride*, $AsCl_3,2C_2H_2$, is readily formed as a heavy, yellow oil, D^{15} 1·6910, b. p. 250°. Its vapours are strongly irritating, but not markedly poisonous, although exhibiting strong bactericidal power. When compared with the corresponding antimony and aluminium compounds, the arsenic

derivative exhibits a remarkable stability, since it can be distilled and is not decomposed by water. When heated with potassium hydroxide solution, it evolves acetylene. At a higher temperature, arsenic trichloride and acetylene in the presence of aluminium chloride yield a black, *organo-arsenic compound* of high molecular weight which is very stable towards reagents, but sensitive to light, and in its properties resembles the aluminium derivative prepared by Baud in a similar manner; it contains 7·70% As, 69·25% C, 5·18% H, and 7·87% O. [Total, 90% only.] H. W.

Organo-metallic Compounds. II. The Action of Carbon Monoxide on Sodium Alkyls. HANS HEINRICH SCHLUBACH (*Ber.*, 1919, **52**, [*B*], 1910—1914).—Carbon monoxide is readily absorbed by mixtures of sodium and mercury diethyl or mercury diphenyl in light petroleum or benzene, that is, by the organo-sodium compounds (compare Schlenk, A., 1917, i, 255). In the case of sodium ethyl the products are diethyl ketone, triethylcarbinol, and propionic acid, whilst the smoother reaction in the case of sodium phenyl gives rise to benzophenone (30%), triphenylcarbinol (25%), and benzoic acid (16%), the yields being calculated on the weight of mercury diphenyl used. J. C. W.

*cyclo***Pentadiene and its Dimeride.** HANS STOBBE and FRITZ DÜNNHAUPT (*Ber.*, 1919, **52**, [*B*], 1436—1442).—From the result of refraction measurements made a few years ago, Stobbe concluded that *cyclo*pentadiene changes almost completely into a dimeride within thirty days at 20° (A., 1912, i, 842). The nature of the atmosphere above the oil, whether air or carbon dioxide, seemed to have no great influence on the rate at which the refractive index rose. Inasmuch as the hydrocarbon, and especially its dimeride, spontaneously absorb oxygen, it remained to be proved whether the polymerisation is accompanied by autoxidation. It is actually found that the end-product of the polymerisation when the oil is freely exposed to oxygen is not the dimeride, but its di-peroxide, probably represented by the annexed formula. In the absence of oxygen, the end-product has a *slightly* greater refractive index. The rate at which polymerisation proceeds is distinctly, but only very slightly, greater in the light than in the dark. J. C. W.



The Benzene [Formula] Problem. II. A. VON WEINBERG (*Ber.*, 1919, **52**, [*B*], 1501—1508).—See this vol., ii, 14.

Catalytic Oxidation of Benzene. JOHN M. WEISS and CHARLES R. DOWNS (U.S. Pat. 1318633).—Benzene is oxidised to compounds containing hydrogen, oxygen, and less than six carbon atoms by the action of a gas containing oxygen at a temperature of 300—500° in the presence of a catalyst. G. F. M.

Oxidation of Side-chains with Potassium Permanganate. LUCIUS A. BIGELOW (*J. Amer. Chem. Soc.*, 1919, **41**, 1559—1581).—The action of potassium permanganate in alkaline solution on three nitrotoluenes has been investigated. The experiments were generally performed by gradually adding the solid permanganate to a boiling suspension of the nitrotoluene in aqueous sodium hydroxide solution; in the case of *p*-nitrotoluene, oxidation was also effected at lower temperatures, but the yields were considerably decreased and the duration of the experiments greatly prolonged.

Changes in the conditions of oxidation, in general, merely cause a different proportion of the nitrotoluene to be attacked by the oxidising action, the ratio of nitrobenzoic acid produced to unchanged nitrotoluene remaining essentially constant. The conclusions are therefore drawn that the quantity of nitrotoluene or nitrobenzoic acid entirely destroyed by the oxidising agent is practically constant and almost independent of the oxidation procedure, and that at least two entirely independent actions take place simultaneously in the oxidising mixture, namely, the oxidation of the organic compound and the decomposition of the permanganate into manganese oxides and free oxygen. It is somewhat curious to note, however, that solutions containing alkali and permanganate, in the proportions most frequently used in this work, do not decrease in oxidising power when boiled for protracted periods in the absence of organic matter.

Increase in the concentration of the alkali in the oxidising mixture up to a certain point favours the oxidation of *o*-nitrotoluene, beyond which point a further increase produces essentially no effect, all other conditions being kept constant. By this increase in alkaline concentration, the oxidation of the meta-isomeride is hindered, such oxidation being most effective in an essentially neutral medium; with *p*-nitrotoluene, oxidation is favoured up to a certain point, beyond which the quality of the product becomes very poor. Possibly, acceleration of the oxidation of the ortho- and para-isomerides by alkali is due to their conversion into a quinonoid form, which is impossible with the meta-derivative.

Increasing dilution of the reaction mixture favours the oxidation of all the nitrotoluenes, probably owing to retardation of the decomposition of the permanganate into manganese oxides and oxygen.

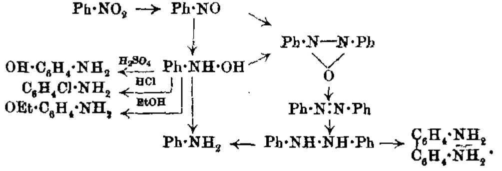
In all circumstances, *p*-nitrotoluene is oxidised most readily, the ortho-compound next, and the meta-isomeride least readily.

Catalytic influences have been studied by carrying out the oxidations of *o*- and *p*-nitrotoluenes in iron, copper, and enamel-lined vessels respectively. In both cases nearly the same results were obtained in the copper and enamel-lined containers, but distinctly lower yields and products of poorer quality in the iron vessel both with and without alkali. The addition of salts of calcium and magnesium to the reaction mixture in the oxidation of *p*-nitrotoluene in neutral solution produced no noticeable effect, and a similar result was obtained after addition of pyridine to a similar oxidation in alkaline solution, although it acts as a powerful negative catalyst in certain permanganate reactions.

A practical method for the preparation of *m*-nitrotoluene has been elaborated, consisting in the nitration of aceto-*p*-toluidide to *m*-nitroaceto-*p*-toluidide, hydrolysis of the acetyl group, and elimination of the amino-group; the details are fully discussed in the original paper. H. W.

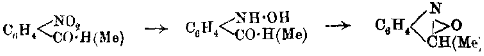
Production of Benzyl Chloride and Benzylidene Chloride and of certain Homologues and Substitution Products of these Compounds. LEVINSTEIN, LTD., HERBERT LEVINSTEIN, and WALTER BADER (Brit. Pat. 134250).—Substitution products containing chlorine in the side-chain are obtained by treating hydrocarbons at temperatures below 0° with hypochlorous acid in aqueous solution. For example, toluene (3 mols.) is emulsified with a hypochlorite solution containing 1 mol. of active chlorine, and after cooling to −5° dilute sulphuric or other acid (1 equivalent) is gradually added. The product, containing unchanged toluene, 60—70% of the theoretical quantity of benzyl chloride, and small quantities of benzylidene chloride and higher chlorinated products, is purified by fractional distillation. A second atom of chlorine may be similarly introduced, it occupying preferably a position in the methyl group already substituted if more than one are present. Monochlorotoluenes behave similarly, but the higher chlorinated toluenes, nitro-substitution products, sulphonyl chlorides, and cresol esters do not give side-chain substitution products under these conditions. Sulphonic acids are substituted in the nucleus.
G. F. M.

Determination of the Course of the Reaction in the Catalytic Reduction of Nitrobenzene. F. F. NORD (*Ber.*, 1919, **52**, [*B*], 1705—1712).—In the reduction of nitrobenzene by chemical or electrical means, it is evident that phenylhydroxylamine plays an important part, as the following scheme indicates:



It appeared to be of interest, therefore, to determine whether it is formed during the catalytic reduction of nitrobenzene by means of colloidal platinum protected by gum arabic, but this mode of reduction offers very little scope for controlling the rate of the reaction and isolating any intermediate products, compared with the electrolytic method. To surmount this difficulty, the reduction of *o*-nitrobenzaldehyde and *o*-nitroacetophenone was tested, for the aldehyde or ketone group in the ortho-position is capable of form-

ing anthranils through condensation with the hydroxylamine group thus:



(compare Bamberger and others, A., 1904, i, 93; 1909, i, 509, 511). By stopping the reaction after two molecular proportions of hydrogen were absorbed, the anthranils could, indeed, be isolated.

The rate at which nitrobenzene is reduced to aniline is practically constant, and so it is during the reduction of *o*-nitroacetophenone to *o*-aminoacetophenone, the yields being quantitative. In the case of *o*-nitrobenzaldehyde, however, there is a very considerable lag after the anthranil stage is reached. The absorption of the third molecular proportion of hydrogen takes about twelve times as long and the product contains only a small quantity of *o*-aminobenzaldehyde. The chief product is Friedländer and Göhring's pale yellow condensation product of *o*-aminobenzaldehyde, m. p. 183—186° (A., 1884, 1019). J. C. W.

The Nitrotoluenes. I. Binary Systems of a Nitrotoluene and *s*-Trinitro-*m*-xylene. JAMES M. BELL and JAMES P. SAWYER (*J. Ind. Eng. Chem.*, 1919, **11**, 1025—1028).—Determinations have been made of the freezing points of binary systems in which one component was 2:4:6-trinitro-*m*-xylene and the other a nitrotoluene, and also of ternary systems containing two of these nitrotoluenes and 2:4:6-trinitro-*m*-xylene. The cooling-curve method was used for the determinations. In the case of mixtures of trinitro-*m*-xylene with the nitrotoluenes the eutectic temperatures (corr.) were as follows: with 2:4:6-trinitrotoluene, 74·8° (corresponding with 8% of the trinitroxylene); with 2:4-dinitrotoluene, 67·7° (corresponding with 6% of trinitroxylene); and with *p*-nitrotoluene, 50·5° (corresponding with 2%). The binary eutectic temperature for the mono- and dinitro-toluenes (26·4°) was lowered to 25·7° by the addition of trinitroxylene, and a similar lowering was observed on adding trinitroxylene to binary mixtures of the other nitrotoluenes. The relationship between the composition and m. p. of mixtures is shown by the equation $\log_e x = -Q(T_0 - T)/RTT_0$, where Q represents the molecular heat of fusion, T_0 is the m. p. of the pure substance, T its m. p. in the presence of a second component, and x the molecular fraction of the melting component. The value of Q calculated from the points on the curve for trinitro-*m*-xylene and trinitrotoluene, $x = 0·337$ and $T = 138·1°$ C. or 411·1° A., was found to be 9200 cals. Substitution of these values in the above equation gave $T = 2012·7/4·424 \log_{10} x$. This gave results agreeing well with the observed results in the case of mononitrotoluene, but in the case of the other two nitrotoluenes there was considerable deviation for the eutectic mixtures up to about 20% of trinitro-*m*-xylene. C. A. M.

The Nitrotoluenes. II. Refractive Indices of Mixtures of *p*-Nitrotoluene, 2 : 4-Dinitrotoluene, and 2 : 4 : 6-Trinitrotoluene. JAMES M. BELL and EDMUND O. CUMMINGS (*J. Ind. Eng. Chem.*, 1919, **11**, 1028—1029).—The refractive indices of mixtures of *p*-nitrotoluene, dinitrotoluene, and trinitrotoluene were determined at 38—39°, and the results expressed in relation to the composition of the mixtures in a triangular diagram showing the lines of equal refractive index. The results, which were confined to mixtures freezing below 40° (the eutectic temperatures being about 17°), agreed in all but a few instances (within the limits of experimental error) with the values calculated by means of the formula $n = 1{\cdot}542m + 1{\cdot}572d + 1{\cdot}580t$, where m, d, and t represent the respective weights of mono-, di-, and tri-nitrotoluene in a mixture. C. A. M.

The Conductivities of Iodoanilinesulphonic Acids. (MISS) MARY BOYLE (T., 1919, **115**, 1505—1517).

Preparation of [Derivatives] of *p*-Toluenesulphonic Acid Halogenated in the Side-chain. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (D.R.-P. 312959; from *Chem. Zentr.*, 1919, iv, 373—374). —*p*-Toluenesulphonic acids or their dry salts are treated at an elevated temperature with halogens or substances which yield halogens, and in the presence or absence of halogen carriers. ω-Chloro- or di-ω-chloro- or ω-bromo- or di-ω-bromo-toluene-*p*-sulphonic acids are obtained according to the amount of halogen used and the experimental conditions employed. The *sodium* salts of ω-chlorotoluene-*p*-sulphonic acid and ω-*o*-dichlorotoluene-*p*-sulphonic acid are particularly described. H. W.

New Halogenated Sulphones. A. PURGOTTI (*Ann. R. scuola superiore d'agr. in Portici*, 1915—1916, (2), **13**, 8 pp.).—The sulphones were obtained by the action of alkyl or aryl haloids on a boiling alcoholic solution of sodium *p*-chlorobenzenesulphinate for fourteen to twenty hours. Thus, methyl iodide yields p-*chlorophenylmethylsulphone*, slender, needle-shaped, vitreous crystals, m. p. 57—58°, which is not reduced by nascent hydrogen or oxidised by permanganate. Ethyl bromide yields p-*chlorophenylethylsulphone*, white crystals, m. p. 260—261° (decomp. at a slightly higher temperature), which is very stable to oxidising and reducing agents. *iso*Propyl bromide yields p-*chlorophenyl*iso*propylsulphone*, vitreous prisms, m. p. 226—227°, which is unaltered by oxidising or reducing agents. Ethylene dibromide yields *di*-p-*chlorophenylethylenedisulphone*, silky laminæ, m. p. 237—238°, which is not attacked by oxidising agents, but is converted into 2 mols. of *p*-chlorophenyl methyl sulphone by zinc and hydrochloric acid. p-*Chlorophenylbenzylsulphone*, prepared from benzyl chloride, forms white laminæ, and has m. p. 257—258°; oxidising agents change it into benzoic acid and *p*-chlorobenzenesulphonic acid. p-*Chlorophenyl*-2 : 4 : 6-*trinitrophenylsulphone*, pre-

pared from picryl chloride, forms a dense, brownish-red oil, which, after twenty-four hours, solidifies to a crystalline mass; after re-crystallisation, this forms yellow, lustrous needles, m. p. 104—105°. If heated slowly it decomposes at about 200°, but if heated quickly explodes violently. CHEMICAL ABSTRACTS.

A Method for the Preparation of Aromatic Selenonic Acids. *o*- and *p*-Xyleneselenonic Acids. RICHARD ANSCHÜTZ JOSEF KALLEN, and KARL RIEPENKRÖGER (*Ber.*, 1919, **52**, [*B*], 1860—1875).—The xylenes react with 96% selenic acid (the preparation of which is described) in the presence of acetic anhydride at 0°, giving white crystals of the very hygroscopic selenonic acid. The position of the substituent has not been determined, but it is probable that one compound is p-*xylene-2-selenonic acid*, m. p. 95—96°, and the other o-*xylene-4-selenonic acid*, m. p. 108—110°. Salts of ten metals are described, as well as the corresponding salts of the sulphonic acids, most of which are new. Most attention is paid to the molecules of water of crystallisation, the numbers of which are set out in the following table:

Acid.	NH_4.	K.	Na.	Ba.	Mg.	Zn.	Ag.	Cu.	Ni.	Co.
p-Xyleneselenonic......	0	0	4	3	8	10	1	10	7	9
,, sulphonic ...	0	1	1	0	8	10	1	5	7	9
o-Xyleneselenonic ...	0	0	4	3	0	6	0	6	5	5
,, sulphonic ...	0	0	5	2	5	5	0	6	6	5

J. C. W.

ωω′-Diarylparaffins and ω-Arylparaffincarboxylic Acids. W. BORSCHE (*Ber.*, 1919, **52**, [*B*], 2077—2085).—The author has applied Clemmensen's method of reduction to a number of mono- and di-ketones which had previously served as starting point in the preparation of ωω′-diarylparaffins (Borsche and Wollemann, A., 1913, i, 171). In general, it is found that αβ-unsaturated ketones yield only small quantities of the corresponding saturated hydrocarbons when reduced by amalgamated zinc and concentrated hydrochloric acid, large amounts of resin being formed. The corresponding saturated mono- and the saturated di-ketones, on the other hand, give satisfactory yields of the hydrocarbons. The method may also be successfully employed in the reduction of a number of ketonic acids.

αε-Dianisylpentane, a colourless, oily liquid, b. p. 264—266°/30 mm., is prepared by the reduction of αε-di-*p*-methoxyphenylpentane-γ-one by zinc and hydrochloric acid; the corresponding *phenol*, b. p. 300—301°/32 mm., is obtained by the reduction of *αε-di*-p-*hydroxyphenylpentan-γ-one*, colourless oil, b. p. 313—314°/14 mm., and yields a *tetranitro*-derivative, pale yellow crystals, m. p. 146—148° (decomp.). *αζ-Di*-m-*4-xylylhexane* forms colourless leaflets, m. p. 76—77°, b. p. 247—248°/20 mm. (formed from *αζ-di*-m-*4-xylylhexane-αζ-dione*, colourless needles, m. p. 125—126°, which results, together with m-4-*xyloylvaleric acid*, colourless needles, m. p. 98—99°, from the condensation of adipyl chloride

ith *m*-xylene in the presence of aluminium chloride [compare eckenstedt, *Inaug. Diss.*, Göttingen, 1911]). *aθ-Di*-m-*4-xylyl-tane*, colourless needles, m. p. 63—64°, b. p. 253—254°/13 mm., obtained from *aθ-di*-m-*4-xylyloctane-aθ-dione*, yellow needles, . p. 78—79°. Reduction of *aι-di*-p-*tolylnonane-aι-dione*, slender, olourless needles, m. p. 78—79°, leads to the formation of *aι-di*-p-*lylnonane*, m. p. 48—49°, b. p. 248—252°/18 mm. (ω-p-*toluoyl-toic acid* has m. p. 98°). *aκ-Di*-m-*4-xylyldecane-aκ-dione*, slender, tertwined needles, m. p. 61°, could not be reduced to the corre-onding hydrocarbon by Clemmensen's or Paal's process.

The following acids have been prepared by Clemmensen's method om the ketonic acids or their esters: γ-p-*tolyl*-n-*butyric acid*, lourless leaflets, m. p. 58—59°, from β-*p*-toluoylpropionic acid; *β-naphthyl*-n-*butyric acid*, colourless leaflets, m. p. 100° (*ethyl* ter, colourless oil, b. p. 216—218°/20 mm.); *ε-phenylhexoic acid*, p. 206—208°/30 mm.; *η-phenyloctoic acid*, colourless leaflets, p. 209—210°/14 mm.; *ι-phenyldecoic acid*, m. p. 41°, b. p. !8—230°/18 mm. (*ethyl* ester, b. p. 220—224°/20 mm.). It should noted that in the reduction of the acids with amalgamated zinc id hydrochloric acid in the presence of a relatively small amount alcohol, esterification of the organic acid frequently occurs to me extent.

The following products have been obtained from adipyl chloride id toluene, *p*-xylene, and mesitylene respectively: *aζ-di*-p-*tolyl-xane-aζ-dione*, m. p. 144—145°, and *δ*-p-*toluoylvaleric acid*, m. p. 3—154°; *aζ-di*-p-*3-xylylhexane-aζ-dione*, m. p. 127—128°, and p-*3-xyloylvaleric acid*, m. p. 132—133°; *aζ-dimesitylhexane-aζ-one*, m. p. 102—103°, and *δ-mesitoylvaleric acid*, crystalline mass, p. 236°/13 mm. Glutaryl chloride and *m*-xylene yield *aε-di*-*4-xylylpentane-aε-dione*, m. p. 60—61°, and γ-m-*xyloylbutyric id*, m. p. 118°. H. W.

Preparation of Nitro-compounds of Tetrahydronaphthalene and its Homologues. TETRALIN G.M.B.H. (D.R.-P. 9014; from *Chem. Zentr.*, 1919, iv, 374).—Tetrahydro-phthalene, or its homologues, is treated with nitric-sulphuric acid other nitrating mixtures which do not contain more than 25% water in such a manner that the temperature does not exceed ° in the first phases of the action. In these circumstances, oxida-on and resinification are almost completely avoided. Tetrahydro-phthalene and nitric-sulphuric acids give a mixture of *a*- and *nitrotetrahydronaphthalene*, b. p. 121—128°/0·17 mm., which is so obtained when concentrated nitric acid (D 1·47) is gradually ded to a solution of tetrahydronaphthalene in acetic anhydride, mixture of acetic acid and acetic anhydride, or an indifferent lvent. A mixture of nitric acid (D 1·47, 160 parts) and sulphuric id monohydrate (200 parts) yields 1 : 3-*dinitrotetrahydro-phthalene*, yellow crystals, m. p. 71—72°, which is oxidised to *5-dinitrophthalic acid*, m. p. 226°, by moderately concentrated tric acid. It decomposes when heated, and forms an explosive

mixture with potassium chlorate, ammonium nitrate, etc. It is converted by a mixture of fuming sulphuric and nitric acids into *trinitrotetrahydronaphthalene*, yellowish-white crystals, m. p. 80—81°. H. W.

Triphenylmethyl. XXIX. Diphenyl-α-naphthylmethyl. M. GOMBERG and C. S. SCHOEPFLE (*J. Amer. Chem. Soc.*, 1919, **41**, 1655—1676. Compare A., 1918, i, 111).—The investigation was undertaken with the object of preparing a compound possessing a considerably greater degree of dissociation than triphenylmethyl to determine whether this attribute would be accompanied by an enhancement of the various chemical characteristics of the latter, and to determine with a high degree of accuracy the molecular weight of the free radicle in various solvents covering a wide range of temperature in order to ascertain the influence of temperature on the molecular state of the free radicle.

Diphenyl-α-naphthylmethyl chloride, large, colourless crystals, m. p. 170—171°, is most conveniently prepared by the action of the calculated quantity of acetyl chloride on diphenylnaphthylcarbinol dissolved in benzene; the corresponding *bromide* has m. p. 165—166° (slight decomp.), whilst *diphenylnaphthyl ethyl ether* forms well-defined, colourless crystals, m. p. 132°. *Diphenyl-α-naphthylmethyl* is obtained by the action of molecular silver on a solution of the chloride in benzene, and forms practically colourless crystals, which gradually become pale yellow, m. p. about 135—137° after darkening at 130°. The radicle absorbs oxygen very rapidly, but in spite of the fact that the theoretical amount of the gas is absorbed, diphenylnaphthylmethyl, like triphenylmethyl, does not give the theoretical quantity of peroxide. It readily reacts with iodine and an equilibrium is attained, $CPh_2{\cdot}C_{10}H_7 + I \rightleftharpoons CPh_2I{\cdot}C_{10}H_7$, when approximately 60% of the radicle has been changed; attempts to isolate the iodide were unsuccessful, but its formation is definitely established by the isolation of the corresponding *anilide*, m. p. 151°. When an excess of iodine is added to the solution of diphenylnaphthylmethyl, an unstable periodide separates as an oil. When treated with hydrogen chloride in benzene solution, the free radicle is converted to the extent of more than 80% into diphenylnaphthylmethane and diphenylnaphthylmethyl chloride, the remainder being transformed into a *polymeride* $C_{46}H_{34}$, very fine, colourless crystals, m. p. 234—235°, the molecular weight of which appears to be abnormal. Reduction by hydrogen in the presence of platinum black converts diphenylnaphthylmethyl into diphenylnaphthylmethane.

Attempts are described to prepare additive compounds of the free radicle with ethyl and ethyl amyl ethers, amyl formate, ethyl acetate, amyl acetate, ethyl chloroacetate, ethyl valerate, acetone, dipropyl ketone, methyl butyl ketone, acetonitrile, propionitrile, benzene, toluene, xylene, and hexane respectively; in no case did addition take place, the behaviour of diphenylnaphthylmethyl in this respect being in marked contrast with that of triphenylmethyl.

Solutions of diphenylnaphthylmethyl are only slowly affected by exposure to light; since, however, the products formed contain considerable quantities of diphenylnaphthylmethane, it seems probable that the reaction occurs on lines similar to those with triphenylmethyl, but far more slowly.

The molecular weight of diphenylnaphthylmethyl has been determined by the cryoscopic method in nitrobenzene, *p*-bromotoluene, *p*-dichlorobenzene, *p*-chlorobromobenzene, and naphthalene respectively, thus giving a temperature range from +6° to 80°; it has been found that the temperature as well as the concentration has a marked influence on the dissociation of free radicles, whilst the nature of the solvent appears to exert but slight influence. Increase in the concentration of the solution invariably causes an increase in the molecular weight, which is interpreted as shifting the equilibrium, $C_{10}H_7{\cdot}CPh_2{\cdot}CPh_2{\cdot}C_{10}H_7 \rightleftharpoons 2C_{10}H_7{\cdot}CPh_2$, in favour of the bimolecnlar form. At a temperature of about 60°, diphenylnaphthylmethyl is shown to be present entirely in the unimolecular form, bnt above this temperature the molecular weight suffers a further decrease, the cause of which has not been established. H. W.

The Fluorene Series. I. ADOLF SIEGLITZ (*Ber.*, 1919, **52**, [*B*], 1513—1517).—Thiele has shown that fluorene condenses with benzaldehyde, anisaldehyde, cinnamaldehyde, and furfuraldehyde in the presence of sodium ethoxide (A., 1900, i, 347; 1906, i, 571). Derivatives of other aldehydes are now described.

9-o-*Methylbenzylidenefluorene* forms flat, colourless needles and prisms, m. p. 109·5°, soluble in concentrated sulphuric acid with violet colour; *picrate*, orange needles, m. p. 138—139°. 9-p-*Methylbenzylidenefluorene* forms flat, colourless crystals, m. p. 97·5°; *picrate*, yellow, m. p. 117—118°. 9:9′-*Terephthalylidenedifluorene*, $C_6H_4(CH{:}C_{13}H_8)_2$, crystallises in golden-yellow, glistening leaflets, m. p. 209—210°, olive-green in sulphuric acid. The 9-*chlorobenzylidenefluorenes* are as follows: *ortho*, yellow needles, m. p. 176°, dark brown in sulphuric acid; *meta*, pale yellow prisms and pyramids, m. p. 90·5°, deep green in sulphuric acid; *para*, pale yellow, m. p. 149·5°, deep blue in sulphuric acid. 9-m-*Bromobenzylidenefluorene* forms yellow needles, m. p. 92—93°, deep green in sulphuric acid. J. C. W.

Transformation of Anilines into *cyclo*Hexylamines and the Isomerism of these Bases. A. SKITA and W. BERENDT (*Ber.*, 1919, **52**, [*B*], 1519—1535).—Hitherto, the catalytic reduction of anilines has given very unsatisfactory results, for there is a great tendency for ammonia to be evolved and secondary amines to result in consequence. With colloidal platinum as the catalyst, however, and by varying the concentration, temperature, and proportion of hydrochloric acid present, it is possible so to control the reduction that the primary *cyclo*hexylamine is the sole product or the secondary base the main product. Reduction with colloidal platinum is about thirty times as rapid as with spongy platinum,

which is probably due, not only to the greater surface available, but to the fact that the bases have no time to "poison" the catalyst before the action is over. In any case, the catalyst must be employed in unusual concentrations, about 0·6% for the monoamines and double this for diamines.

The catalyst is prepared by shaking a solution of hydrochloroplatinic acid, containing gum arabic, with hydrogen, after inoculation with a little colloidal platinum.

The following reductions are described. *Aniline:* A mixture containing 1·5 grams of platinum (from hydrochloroplatinic acid), 1·5 grams of gum arabic, 0·09 mol. (8·37 grams) of aniline, 110 c.c. of glacial acetic acid, and 120 c.c. of water (designated the "normal mixture"), was reduced in three hours at 21°, giving *cyclo*hexylamine, b. p. 135° (40·3%), and di*cyclo*hexylamine, b. p. 250° (59·7%). At 55—60° the same mixture was reduced in twenty-five minutes, the yield of secondary base being 78·4%. With the addition of 10 c.c. of concentrated hydrochloric acid, the mixture was reduced in two and a-half hours at 21°, giving primary *cyclo*hexylamine only. *Alkylanilines:* At about 40—50° good yields of the simple secondary amines are obtained, but at 80°, and with more concentrated solutions of the catalyst, the monoalkylanilines give 40—55% yields of tertiary amines. The dialkylanilines give almost the same results under both conditions. cyclo*Hexylmethylamine*,

$$C_6H_{11}\cdot NHMe,$$

has b. p. 145—147°, and its *benzoyl* derivative has m. p. 85—86°; *cyclo*hexyldimethylamine has b. p. 160—161° (A., 1904, i, 661); *cyclo*hexyldiethylamine has b. p. 193° (*ibid.*), *di*cyclo*hexylmethylamine* has b. p. 265°, and its lemon-yellow *picrate* has m. p. 140°; *di*cyclo*hexylethylamine* has b. p. 268°, and its *picrate* has m. p. 138°.

Toluidines.—The "normal mixture," containing *p*-toluidine, plus 5 grams of hydrogen chloride, was reduced at 25° in four hours, the product being 4-methyl*cyclo*hexylamine, b. p. 150—151° (Gutt, A., 1907, i, 508). This is apparently a mixture of *cis*- and *trans*-isomerides, for it yields two *benzoyl* derivatives, the *α*-form having m. p. 180° (corr.) (*ibid.*), and the *β*-form, which is the more soluble of the two in dilute alcohol, having m. p. 116°. At 52° the "normal mixture" is reduced in seventy-five minutes, giving a 68% yield of 4:4′-*dimethyldi*cyclo*hexylamine*, b. p. 133°/10 mm. This gives two *nitrosoamines*, the *α*-form, m. p. 128—129° (corr.), crystallising from moderately strong alcohol, and the *β*-form, m. p. 90—91° (corr.), from more dilute alcohol. With *m*-toluidine the "normal mixture" was reduced in five hours at 23—26°, to 55·6% of primary amine, and 44·4% of secondary base, but at 55° the absorption of hydrogen was complete in thirty minutes, and the yield of secondary amine was 79·1%. 3-Methyl*cyclo*hexylamine has b. p. 150—151° (*ibid.*), and forms two *benzoyl* derivatives, the *α*-form having m. p. 127° (corr.) and the *β*-form m. p. 98·5° (corr.). 3:3′-Dimethyldi*cyclo*hexylamine has b. p. 172—173° (Wallach, A., 1893, i, 115). In the case of *o*-toluidine the yields with the "normal mixture"

were 83·8% primary and 16·2% secondary amine at 23°, and 58% secondary base at 55°. 2-Methyl*cyclo*hexylamine, b. p. 150—151°, hydrochloride, m. p. 269°, forms two *benzoyl* derivatives, *a*-, m. p. 46° (corr.) (Gutt, *loc. cit.*), and *β*-, m. p. 107° (corr.). 2:2'-*Dimethyldi*cyclo*hexylamine* has b. p. 273—274°, forms a *hydrochloride*, m. p. 284°, and yields two *picrates*, *a*-, tetrahedra, m. p. 84° (corr.), and *β*-, delicate needles, m. p. 153° (corr.).

Nitroanilines.—*m*-Nitroaniline is mainly reduced to *m*-phenylenediamine if insufficient catalyst is used, but a mixture containing 9 grams of base, 4 grams of colloidal platinum, 3 grams of gum arabic, 4 grams of hydrogen chloride, 150 c.c. of glacial acetic acid, and 130 c.c. of water was reduced at 55° so rapidly that heat was developed, and a 62% yield was obtained of *cyclo*hexylene-1:3-diamine, b. p. 193—194°, *platinichloride*, yellow needles (Merling, A., 1894, i, 177). *p*-Nitroaniline, under similar conditions, gave a 45% yield of *cyclo*hexylene-1:4-diamine, b. p. 181°, *platinichloride*, yellow crystals (von Baeyer, A., 1889, 1147).

In most of the reductions the hydrogen is kept under 3 atm. pressure. J. C. W.

Halogenalkylated Aromatic Amines. IV. Julius von Braun and Georg Kirschbaum (*Ber.*, 1919, **52**, [*B*], 1716—1724. Compare A., 1918, i, 107, 269, 406).—When methyl-β-bromoethylaniline is boiled with hydrochloric acid, it is converted into *methyl-β-chloroethylaniline*, $NMePh\cdot CH_2\cdot CH_2Cl$, which is a very pale yellow oil, b. p. 134°/13 mm., and forms a yellow *picrate*, m. p. 107°, a *methiodide*, colourless leaflets, m. p. 125°, and a p-*nitroso*-compound, emerald leaflets, m. p. 69°, which may be oxidised to p-*nitromethyl-β-chloroethylaniline*, $NO_2\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CH_2Cl$, a greenish-brown, crystalline powder, m. p. 90°, and reduced to *methyl-β-chloroethyl*-p-*phenylenediamine*, an oil which yields an *acetyl* derivative, m. p. 131°. The reactivity of the halogen atom is not so great as in the case of the bromo-derivative, but it is still quite considerable. For example, the base reacts with sodium benzoate to form *methyl-β-benzoyloxyethylaniline* [*β-methylanilinoethyl benzoate*], m. p. 48—49° (*picrate*, m. p. 164°), and with ethyl sodiomalonate to give *ethyl β-methylanilinoethylmalonate*, $NMePh\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$, a viscous oil, b. p. 190°/mercury pump.

The replacement of one halogen by another may be illustrated still further. The chloro-derivative yields the bromo-compound when boiled with hydrobromic acid, and both may be converted into *methyl-β-iodoethylaniline*, colourless crystals, m. p. 43—44° (*hydriodide*, m. p. 139°), by boiling with hydriodic acid. The phenomenon has been put to practical use in the preparation of a γ-halogenopropyl base. Methylaniline does not react in the desired way with ethylene or trimethylene dichlorides, and the product obtained by heating it with trimethylene dibromide cannot be distilled. By boiling the crude product with hydrochloric acid, however, the above exchange of halogens takes place, and *methyl-β-*

chloropropylaniline may be isolated as a very pale yellow oil, b. p. 140—144°/13 mm. This base forms a *platinichloride*, m. p. 154—156°, a *picrate*, m. p. 113°, a *methiodide*, m. p. 107—108° and a dark, oily *nitroso*-compound, and it reacts with sodium to give oily *N* : *N'-diphenyldimethylhexamethylenediamine*,

$$NMePh\cdot[CH_2]_6\cdot NMePh$$

(*picrate*, m. p. 82°), and with trimethylamine to form the oily *quaternary chloride*, $NMePh\cdot C_3H_6\cdot NMe_3Cl$ (*platinichloride*, m. p. 211°). When boiled with hydrobromic acid, *methyl-β-bromopropylaniline* is formed, and this may now be distilled; b. p. 150—155°/12 mm., 117—121°/0·01 mm.; *picrate*, m. p. 94—95°; *platinichloride*, m. p. 132°.

The halogenoethyl bases yield 1-methyldihydroindole when heated with aluminium chloride, but the halogenopropylanilines do not give quinoline derivatives. J. C. W.

Mechanism of the Grignard Reaction. JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1919, **52**, [*B*], 1725—1730).—In the first communication on bromoalkylated anilines (A., 1918, i, 107) it was shown that the magnesium compounds react with aldehydes and ketones, but that the ketones are regenerated on treating the products with water. It was suggested that the primary products can be represented thus:

$$\begin{matrix}R\\H\end{matrix}\!\!>C\vdots O<\!\!\begin{matrix}MgX\\R'\end{matrix} \quad\text{and}\quad R_2\vdots C\vdots O<\!\!\begin{matrix}MgX\\R'\end{matrix}.$$

Apparently, then, when R' is $NMePh\cdot CH_2\cdot CH_2-$, rearrangement into $RR'CH\cdot O\cdot MgX$ is possible in the case of aldehydes, but there are steric hindrances in the way of the formation of $R_2R'C\cdot O\cdot MgX$. When the heavy NMePh-group is further away, however, as in the case of methyl-γ-bromopropylaniline (preceding abstract), the necessary rearrangement is possible even in the ketone series.

The following compounds are obtained from magnesium γ-methylanilinopropyl bromide: (1) with *iso*valeraldehyde, N : N'-diphenyldimethylhexamethylenediamine (*ibid.*), and *methyl-δ-hydroxy-ζ-methylheptylaniline*, $NMePh\cdot C_3H_6\cdot CH(OH)\cdot CH_2\cdot CHMe_2$, a viscous oil, b. p. 154—156°/12 mm. (*picrate*, m. p. 161°; *platinichloride*, m. p. 210°); with acetone, methylpropylaniline, and *methyl-δ-hydroxy-δ-methylamylaniline*, a very viscous oil, b. p. 164—170°/13 mm. (*platinichloride*, m. p. 193°); with *cyclo*hexanone, the base,

$$\begin{matrix}NMePh\cdot C_3H_6\\HO\end{matrix}\!\!>C<\!\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>CH_2,$$

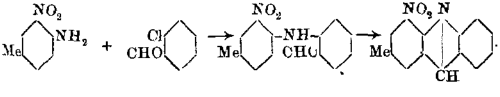
which seems to lose water slowly on heating.

The steric hindrance seems to be connected with the presence of nitrogen also, for the Grignard compound from γ-phenyl-*n*-butyl bromide (A., 1913, *i*, 612) behaves quite normally with acetone, yielding *sec.*-butylbenzene and βη-diphenyloctane (*ibid.*), but chiefly *ε-phenyl-β-methylhexan-β-ol*, $CHMePh\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH$, a very viscous liquid, b. p. 135°/11 mm. J. C. W.

5-Nitro-2-amino-1-methyl-4-*iso*propylbenzene. C. E. ANDREWS (U.S. Pat. 1314923).—To introduce a nitro-group into aminocymene in a position para to the amino-group, the amino-group is first protected against the action of the nitrating medium by boiling with glacial acetic acid for fifteen to twenty hours. Nineteen parts of the solid acetylaminocymene thus obtained are dissolved in 98% sulphuric acid (84 parts) and the solution thus formed is nitrated with a mixture of 98% sulphuric acid (13 parts) and 70% nitric acid (10 parts), while the reacting substances are kept at 0°. By pouring the products into water containing ice a yellow precipitate of *p*-nitroacetylaminocymene is obtained. This may be treated directly for reduction of the nitro- to the amino-group by heating with iron and hydrochloric acid, and the acetyl group may subsequently be removed by treatment with concentrated hydrochloric acid, from which, on keeping, the hydrochloride of 2:5-diamino-1-methyl-4-*iso*propylbenzene separates as crystals. The intermediate product (5-amino-2-acetylamiuo-1-methyl-4-*iso*propylbenzene) may be diazotised and coupled with a hydroxy-aromatic compound in alkaline solution, after which the acetyl group can be removed and the 2-amino-group can then be caused to react with hydroxy- or amino-aromatic compounds. This procedure is preferable to reacting on tetrazotised diaminocymene with aromatic hydroxy-derivatives, where two different second components are to be employed in producing bisazo-dyes. CHEMICAL ABSTRACTS.

4-Amino-5-methyl-2-*iso*propylbenzenesulphonic Acid. C. E. ANDREWS (U.S. Pat. 1314927).—Aminocymene or its sulphate is heated for about ten hours with 98% (or fuming) sulphuric acid at about 205° until a test portion gives no reaction for the free amine on making it alkaline. The solid reaction mass is broken up and dissolved in hot sodium hydroxide solution, purified by filtration through "decolorising carbou," and acidified to obtain 4-*amino*-5-*methyl*-2-*iso*propylbenzenesulphonic acid. CHEMICAL ABSTRACTS.

Action of *o*-Chlorobenzaldehyde on Chloroanilines and Amines of Fluorene and Anthraquinone. FRITZ MAYER and IRENE LEVIS (*Ber.*, 1919, **52**, [*B*], 1641—1652).—It has already been found that under certain conditions *o*-chlorobenzaldehyde does not react with ortho-substituted anilines to form the usual azomethines, but condenses according to the following scheme, taking an actual example (A., 1918, i, 36):



The reaction with chloroanilines and aminofluorenes has now been

examined, but these are found to give only the azomethines or ı condensation products at all. Certain anthraquinone derivativ(however, yield the more complex products.

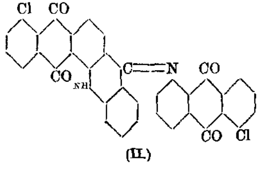
In the experiments, the azomethines were obtained by condensiı the components in warm dilute alcohol, and the other condensatioı were tested by heating the substances in nitrobenzene (naphthalene at 210—220° with a little copper powder an anhydrous sodium carbonate

The chloroanilines gave the following compounds: 2:2′-*dichlor. benzylideneaniline*, m. p. 112—113°; 3:2′-*dichlorobenzyliden aniline*, two forms, m. p. 104° and m. p. 39—40°, the former pas ing into the latter on fusion and inoculation with crystals of th low melting form; 4:2′-*dichlorobenzylideneaniline*, m. p. 65—68° 2:4:2′-*trichlorobenzylideneaniline*, m. p. 97—98°; a *trichloro-2 chlorobenzylideneaniline*, m. p. 109°, from technical trichlorc aniline, the pure 2:4:6-trichloroaniline giving no condensatioı product. 2-Chloro-4-nitroaniline yields 2:2′-*dichloro-4-nitrobenzyl ideneaniline*, yellow crystals, m. p. 155—156°. 4-Chloro-2-nitro aniline only reacts in naphthalene solution, and then gives a smal yield of 3-*chloro-1-nitroacridine*, pale yellow needles, m. p 219—221°. 3-Chloro-*p*-toluidine gives 2 : 2′-*dichloro-4-methyl benzylideneaniline*, m. p. 68—70°. 2-Chloro-5-nitrobenzaldehyd(and *p*-chloroaniline yield 4:2′-*dichloro-5′-nitrobenzylideneaniline* m. p. 124—125°. 2:4-Dinitroaniline and 1-aminoanthraquinone do not condense with 2-chloro-5-nitrobenzaldehyde. 2-Amino-fluorene and 2-aminofluorenone (Diels, A., 1901, i, 521) yield 2:2′-*chlorobenzylideneaminofluorene*, m. p. 128—129, and 2:2′-*chlorobenzylideneaminofluorenone*, m. p. 153—155°. 1-Nitro-2-amino-fluorene does not react, but 2-nitro-7-aminofluorene (A., 1902, i, 758) forms 2-*nitro-7:2′-chlorobenzylideneaminofluorene*, m. p. 230°.

5-Chloro-1-aminoanthraquinone yields o-5-*chloro-1-anthraquin-onylaminobenzaldehyde* (5-*chloro-1-o-aldehydoanilinoanthraquin-one*) (I), reddish-violet crystals, which condenses with more 5-chloro-1-aminoanthraquinone in boiling nitrobenzene, under the influence of mercuric sulphate, giving the *compound* (II).

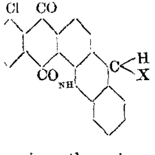
$$C_6H_3Cl{<}{}^{CO}_{CO}{>}C_6H_3\cdot NH\cdot C_6H_4\cdot CHO \longrightarrow$$

(I.)



(II.)

'he aldehyde (I) also condenses to the esters of 1:2-o-*chloro-phthalyl*-5 : 10-*dihydroacridol* (annexed formula), which in the free state is apparently a brownish-violet powder, when heated with sulphuric acid at 115—120°, or with acetic acid saturated with hydrogen chloride. The *hydrogen sulphate* forms dark violet crystals, and the *hydrochloride* is violet.



1-Chloroanthraquinone-2-aldehyde (Ullmann, A., 1916, i, 484) condenses with -aminoanthraquinone to form 1:1'-*anthraquinonylaminoanthra-uinone-2-aldehyde*,

$$C_6H_4<\substack{CO\\CO}>C_6H_3\cdot NH\cdot C_6H_2(CHO)<\substack{CO\\CO}>C_6H_4,$$

; a violet-red powder, which condenses further with 1-amino-ıthraquinone to give a violet *compound* of the formula

$$C_6H_4<\substack{CO\\CO}>C_6H_2<\substack{NH\\-C-}>C_6H_2<\substack{CO\\CO}>C_6H_4$$
$$\| \quad N\cdot C_6H_3<\substack{CO\\CO}>C_6H_4$$

eated with sulphuric acid, the aldehyde also forms the violet *lphonate* of 1:2:8:9-*diphthaloyl*-5 : 10-*dihydroacridyl hydrogen lphate*,

$$\left[C_6H_4<\substack{CO\\CO}>C_6H_2<\substack{NH\\CH}>C_6H_2<\substack{CO\\CO}>C_6H_4\right]_2,H_2SO_4.$$
$$\qquad SO_3H$$

J. C. W.

Diphenylamine. H. ROGERS (U.S. Pat. 1314538).—Diphenyl-nine is formed by heating a mixture of aniline with about 1% ammonium bromide in an autoclave, preferably for about forty-ght hours under a condensing column, which is arranged to ·rmit release of the ammonia evolved without loss of aniline. A mperature of about 300° gives the best results. Bromine itself ay be used as a catalyst instead of ammonium bromide, or other omine compounds may be used, for example, aniline hydro-omide, bromobenzene, or magnesium bromide. It is practically sential that about 1% of water should be present in the reaction ne. After heating in the autoclave, the reaction product is frac-›nated. The first fraction, distilling up to 200°, consists mainly of ıchanged aniline, together with a small amount of diphenylamine, .d is stored for re-digestion with a fresh amount of catalyst.

The second fraction, distilling at 200—300°, consists of a mixture of aniline with a larger amount of diphenylamine. The larger part of the diphenylamine can be recovered from this second fraction by redistillation. The main quantity of the diphenylamine produced is collected in the fraction which distils at 300° and above. A tarry residue is left in the still, from which the catalyst may be recovered. An apparatus is described. CHEMICAL ABSTRACTS.

The Isomerism between Real and Pseudo-haloid Salts. A. HANTZSCH (*Ber.*, 1919, **52**, [*B*], 1544—1572).—Two distinct chromoisomerides have been found in the case of certain -onium haloids, especially iodides, and a study of their absorption and transformations has led the author to postulate the following characteristics of real and pseudo-haloids. (1) *The genuine haloids.*—The halogen is in ionic union with the -onium complex, that is, is in the "outer sphere" according to Werner's teaching; the salts are optically identical with their ions. Thus, $[NR_4]X$, $[PR_4]X$, $[AsR_4]X$, $[SR_3]X$, $[OR_3]X$. (2) *The ψ-haloids.*—The halogen is directly united to the central atom; the absorption is much greater than in the case of the normal haloids, and therefore the ψ-forms are often yellow. They are expressed by the old formulæ for the salts, thus, R_4:N–I, etc. The tendency for the normal salts to change into the less stable ψ-forms is favoured by higher temperatures and non-ionising solvents, such as chloroform and *s*-tetrachloroethane, and depends on the nature of the ions. Of the anions, iodine has the greatest effect and chlorine scarcely any. The most effective cations are those in which the central atom is in an unsaturated ring system, as in pyridinium and pyroxonium salts. Next come the most phenylated ions, such as triphenylbenzyl- and triphenylmethyl-phosphonium, but with the alkylated ions, even such as tetrabenzylarsonium, the salts show little tendency to rearrangement. The isomerisation is a time reaction, and therefore a solution in chloroform generally represents an equilibrium, which is displaced not only by rise of temperature, but also by dilution. This suggests participation of the apparently indifferent solvent, and in the case of 1-ethylpyridinium iodide the fact is revealed that both salts form solvates with chloroform, the stable, normal form giving a less stable solvate than the labile ψ-modification. Ionising solvents have absolutely no optical effect on the normal haloids.

These views are chiefly based on a study of 1-ethylpyridinium iodide and 4-methoxy-2:6-dimethylpyroxonium iodide (compare this vol., i, 72). For the practical details, which are accompanied by much discussion, the original should be consulted.

J. C. W.

Attempted Preparation of New Compounds of Nitrogen. H. STAUDINGER and JULES MEYER (*Helv. Chim. Acta*, 1919, **2**, 608—612).—According to Werner's conception, the co-ordination

number of nitrogen is four, so that only four atoms or radicles can be united directly to a nitrogen atom. Should it be possible, however, for the nitrogen atom to be united directly with five groups, it is to be expected that the most stable compounds would be formed when the atom is attached to five carbon atoms. The only known compound of this type is triphenylmethyltetramethylammonium, $CPh_3{\cdot}NMe_4$, described by Schlenk and Holtz (A., 1916, i, 385), the peculiar instability of which is possibly due to the presence of the triphenylmethyl group. The present communication describes a number of unsuccessful attempts to obtain further compounds of similar structure.

The action of dimethylaniline oxide (2 mols.) on diphenylketen (1 mol.) leads to the formation of dimethylaniline and benzophenone, whilst with molar proportions of the reagents the products are dimethylaniline and diphenylketen oxide, the dimethylaniline oxide behaving in each case as an oxidising agent. With phenylcarbimide and dimethylaniline oxide, carbon dioxide, dimethylaniline, and amorphous substances of high molecular weight are formed. Triethylamine, dimethylaniline, and triphenylamine could not be caused to react with diphenyldiazomethane or with phenylazide.

H. W.

A Peculiar Transformation of Methylallylaniline *N*-Oxide. JAKOB MEISENHEIMER (*Ber.*, 1919, **52**, [*B*], 1667—1677).—Methylallylaniline is converted into *methylallylaniline* N-*oxide*,

$$CH_2{:}CH{\cdot}CH_2{\cdot}NPhMe{:}O,$$

by the action of perbenzoic acid in benzene, being isolated as the *picrate*, $OH{\cdot}NPhMe(C_3H_5){\cdot}O{\cdot}C_6H_2(NO_2)_3$, which crystallises in stout, yellow forms, m. p. 121° (decomp.). If the benzene solution is extracted with 10% hydrochloric acid and the extract is carefully mixed with sodium hydroxide, the oxide is liberated as a very soluble, unstable substance, but if the alkaline solution is heated by means of a current of steam it soon becomes turbid, and a very pale yellow, mobile oil distils over. This oil, b. p. 97°/14—16 mm., is shown to be N-*phenylmethyl*-O-*allylhydroxylamine*, $CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}NMePh$, by the following series of reactions, but no explanation of its formation from the isomeric methylallylaniline *N*-oxide is offered. The transformation is conditioned by the allyl group, for no other amine oxides are known to behave in this way. The most convenient way to obtain the oil is to oxidise the methylallylaniline with Caro's acid at 30—35°, extract impurities with ether, and then add concentrated sodium hydroxide and distil in steam.

The oil is hydrolysed by boiling with hydrochloric acid according to the scheme:

$$C_3H_5{\cdot}O{\cdot}NMePh \begin{cases} \nearrow NHMePh + CH_2{:}CH_2{\cdot}CHO \\ \searrow CH_2{:}CH{\cdot}CH_2{\cdot}OH + NMePhCl \longrightarrow C_6H_4Cl{\cdot}NHMe. \end{cases}$$

Of the products, acraldehyde was identified by its odour and conversion into lead acrylate, methylaniline as its somewhat reddish-yellow *picrate*, m. p. 144·5°, and acetyl derivative, *p*-chloromethylaniline as its greenish-yellow *picrate*, m. p. 153°, and acetyl derivative (Chattaway and Orton, T., 1901, **79**, 465), and possibly *o*-chloromethylaniline, a picrate being obtained in bundles of greenish-yellow needles, m. p. 133°. When heated with zinc dust and acetic acid, the oil yields methylaniline and allyl acetate. The latter was hydrolysed, and the alcohol characterised by conversion into *allyl* p-*nitrobenzoate*, m. p. 28°. Reduction by Skita's method (colloidal platinum protected with gum arabic) gives rise to N-*phenylmethyl*-O-*propylhydroxylamine*, an almost colourless oil, b. p. 92—94°/12 mm., which is hydrolysed by dilute sulphuric acid to propaldehyde, methylaniline, and *p*-hydroxymethylaniline.

J. C. W.

Action of Nitrous Acid on β-Phenylhydroxylamine. EUG. BAMBERGER and ALEX. LANDAU (*Ber.*, 1919, **52**, [*B*], 1837—1842).—A more complete study of this subject, with particular reference to the by-products (compare A., 1894, i, 412). Starting with 79·7 grams of phenylhydroxylamine, 86·5 grams of the nitroso-compound, NO·NPh·OH, were obtained as a precipitate. The filtrate was extracted with ether, and the aqueous solution added to β-naphthol in sodium hydroxide, giving a quantity of dye corresponding with 2·9 grams of benzenediazonium hydroxide. The ethereal solution was saturated with ammonia gas, filtered (residue *A*), shaken with 12% ammonia solution (*B*), dried, and evaporated, leaving 0·69 gram of nitrosobenzene. The residue *A* consisted of ammonium salts, chiefly of nitrosophenylhydroxylamine, but also of phenylnitroamine, NO_2·NHPh, the latter salt being also present in solution *B*. The phenylnitroamine was isolated by dissolving *A* in water, adding sodium carbonate and permanganate in the cold to oxidise the nitrosophenylhydroxylamine to nitrosobenzene, filtering, extracting with ether after acidifying, and shaking the extract with dilute ammonia. On evaporating the ammoniacal solution, 0·11 gram of phenylnitroamine was obtained.

The nitroamine is most probably formed by the rearrangement of the nitrosophenylhydroxylamine under the influence of nitrous acid, for when a solution of the potassium salt of the latter is acidified in the presence of sodium nitrite, a trace of nitroamine is produced.

J. C. W.

Phenols as Mordant Dyes. RICHARD MÖHLAU (*Ber.*, 1919, **52**, [*B*], 1730—1734).—Those phenols which are constitutionally capable of forming internally complex salts are found to impart more or less stable shades to mordanted wool, as the following table indicates:

	Al.	Fe.	Cr.
†α-Anthrol	Brown	Brown	Yel.-brown
†β-Anthrol	Yel.-brown	Yel.-brown	Yel.-brown
Catechol	—	*Pale grey	Yel.-grey
1 : 2-Dihydroxynaphthalene.	—	Grey.-brown	Yel.-brown
†1 : 8- ,,	Black	Brown-black	Brown.-black
†Phenanthraquinol	—	—	Red.-brown
1 : 2-Dihydroxyanthracene .	Yel.-brown	Yel.-brown	Yel.-brown
†2 : 3- ,,	Red.-brown	Red.-brown	Red.-brown
Pyrogallol	—	Dark grey	Yel.-grey
Salicylic acid	—	*Pale red	—
2 : 3-Dihydroxynaphthoic acid	—	*Red.-violet	—
Protocatechuic acid	—	*Grey.-violet	Pale grey
Gallic acid	—	,,	Yel.-grey
Methyl gallate	—	,,	Pale grey
†1 : 2-Dihydroxynaphthalene-4-sulphonic acid	Yel.-brown	Yel.-brown	Red.-brown

(1) With the exception of those marked *, the colours are unchanged by light and air after thirty days, and also by boiling with 2% soap solution.

(2) Those marked † give colours which are quite stable towards boiling *N*-hydrochloric acid.

No effect is produced by phenol, α- and β-naphthols, resorcinol, quinol, 1:3- and 2:7-dihydroxynaphthalenes, or *m*- and *p*-hydroxybenzoic acids. J. C. W.

Acetylation of Nitrophenols in Presence of Catalysts. G. E. Hoeffelman (*Proefschrift Delft*, 1919, 134 pp.; from *Chem. Weekblad*, 1919, **16**, 904).—The author has investigated the acetylation of trinitrophenol, *op*-dinitrophenol, *p*-nitrophenol, and *o*-nitrophenol by *acetic anhydride* both in presence and absence of catalysts such as ferric chloride, zinc chloride, concentrated sulphuric acid, and pyridine. The following points are discussed: (1) The nature of the reactions without a catalyst. (2) Are catalytic reactions definite or does inactivity occur? (3) The relationship between reaction constant and amount of catalyst. (4) The cause of inactivity in certain reactions and the determination of a limit when it occurs. (5) The influence of various catalysts on the acetylation of several nitrophenols. W. J. W.

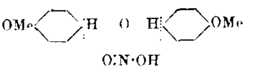
Action of Nitric Acid on Phenolic Ethers. Kurt H. Meyer and Hans Gottlieb Billroth (*Ber.*, 1919, **52**, [*B*], 1476—1489).—It has been known for some time that by-products with very intense colours are formed during the nitration of phenolic ethers. For example, Decker and Salonina isolated a deep blue compound from thymol ethyl ether (A., 1902, i, 767). It is now shown that the substances can be isolated as perchlorates by diluting the nitration products with ice-water, filtering, and adding the solution to perchloric acid. The salts yield diphenylamine derivatives on reduction, and are best regarded (with Decker) as quinonoid salts of substituted diphenylhydroxylamine-*N*-oxides, $NPh_2O{\cdot}OH$.

This is the derivative of nitric acid which corresponds with diphenylarsinic acid, but attempts to isolate it or its metallic salts have been unsuccessful. In the case of the anisyl derivative, the attempts have led to the isolatiou of dianisylnitric oxide,

$$NO(C_6H_4 \cdot OMe)_2,$$

which is more stable than diphenylnitric oxide (Wieland and Offenbächer, A., 1914, i, 955).

In the action of nitric acid on phenolic ethers, there is obviously a choice of two reactions, the ordinary nitration and the present reaction, represented by the annexed formula. Methyl groups, and especially methoxy-groups, in the meta-position are favourable to this reaction, as they are to the coupling process with diazo-compounds, but whilst the phenomenon seems to be most characteristic of phenolic ethers, it is not entirely confined to this class, for resorcinol behaves in a similar manner.



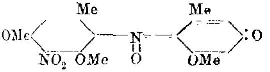
The quinonoid *perchlorate* of *di*-p-*anisylhydroxylamine* N-*oxide*, $OMe \cdot C_6H_4 \cdot N(:O):C_6H_4:O<^{Me}_{ClO_4}$, crystallises from acetone on the addition of light petroleum in coppery needles containing $1H_2O$, which is lost at 50° in a vacuum desiccator. The solutions are red in deep layers and pure blue in thin layers or when very dilute. Reduction to di-*p*-anisylamine may be effected by means of stannous chloride or sodium iodide, and followed titrimetrically in each case. The perchlorate is reduced to *di*-p-*anisylnitric oxide* by treatment with an alkali, or sodium iodide, or zinc powder, in acetone, or, most conveniently, by dissolving it in pyridine and gradually adding water. The oxide crystallises in needles or platelets, and has the appearance of copper powder, m. p. 150° (decomp.). Its reduction by sodium iodide may be followed volumetrically, and it is re-oxidised to the deep violet salts by bromine or concentrated mineral acids.

Phenetole yields the violet-brown *perchlorate* of diphenetylhydroxylamine *N*-oxide, decomp. 114°, and copper-coloured diphenetylnitric oxide. *m*-Tolyl methyl ether gives the *perchlorate* of 5 : 5′-dimethoxydi-*m*-tolylhydroxylamine *N*-oxide, dark crystals with $1H_2O$, decomp. 142°. *o*-Tolyl methyl ether gives a mere trace of coloured salt. *m*-5-Xylyl methyl ether yields the dark brown *perchlorate* of 5 : 5′-dimethoxydi-*m*-2-xylylhydroxylamine *N*-oxide.

Resorcinol dimethyl ether gives the *perchlorate* of 2 : 4 : 2′ : 4′-*tetramethoxydiphenylhydroxylamine* N-*oxide*, $C_{16}H_{18}O_9NCl,H_2O$, as a violet-brown powder, decomp. 178°. The deep green solutions of this become cornflower-blue on adding two equivalents of stannous chloride, and colourless with four equivalents, the final product being 2 : 4 : 2′ : 4′-*tetramethoxydiphenylamine*, which forms large, colourless crystals, m. p. 71°, and yields a *nitroso*-derivative, m. p. 111°. Resorcinol diethyl ether gives the corresponding *perchlorate*,

$C_6H_3(OEt)_2 \cdot N(\dot{:}O)\dot{:}C_6H_3(OEt)\dot{:}OEt \cdot ClO_4$, in very dark green, glistening needles, decomp. 131°.

Orcinol dimethyl ether yields the *perchlorate* of *3:5:3′:5′-tetramethoxydi-*o*-tolylhydroxylamine* N*-oxide*, dark violet-brown needles, $1H_2O$, decomp. 121°, and *3:5:3′:5′-tetramethoxydi-o-tolylamine*, m. p. 106°, and its *nitroso*-compound, m. p. 186°. If the product of the nitration of orcinol dimethyl ether is left with water, a red *compound*, decomp. 150°, is deposited, probably represented by the annexed formula.



Phloroglucinol trimethyl ether gives rise to the *perchlorate* of *2:4:6:2′:4′:6′-hexamethoxydiphenylhydroxylamine* N*-oxide*, dark blue crystals, decomp. 189°. J. C. W.

Aromatic Nitro-derivatives. X. Nitration of Thymol. M. GIUA (*Gazzetta*, 1919, **49**, ii, 158—166).—The author's investigations on the trinitro-compounds obtained on nitrating thymol and its ethyl and methyl ethers confirm the conclusions of Armstrong and Rennie (*Chem. News*, 1883, **47**, 115), Maldotti (A., 1901, i, 80), and Larter (P., 1901, 183), namely, that Lallemand's trinitrothymol and its ethers (*Compt. rend.*, 1857, **37**, 498; 1857, **38**, 1022; 1860, **43**, 375, 459) are in reality trinitro-*m*-cresol and its ethers.

Further, the trinitro-compound obtained by nitrating either the methyl or the ethyl ether of thymol reacts with hydrazine hydrate in alcoholic solution, giving rise to 2:4:6-trinitro-*m*-tolylhydrazine (compare this vol., i, 100). Phenylhydrazine also reacts with these compounds, yielding the same product (compare this vol., i, 98).

Nitration of the ethyl ether of thymol, dissolved in sulphuric acid, by means of fuming nitric acid at a moderately low temperature and for a short time gives the ethyl ether of dinitro-*m*-cresol, m. p. 96—97° (compare Staedel and Kolh, A., 1891, 186). Further nitration of the latter yields the ethyl ether of 4:5:6-trinitro-*m*-cresol, m. p. 75°. In the ethyl ether of dinitro-*m*-cresol obtained from thymol, one of the nitro-groups occupies the position formerly occupied by the *iso*propyl group, which is evidently eliminated by the action of the nitric acid. T. H. P.

Transformation of *cyclo*Hexanones into Catechols. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 30—33).—*Methyl*iso*propylcatechol*, $C_{10}H_{14}O_2$, obtained either as such by heating monobromo-Buchu-camphor above its melting point or as diacetyl derivative by heating the same bromo-compound with acetic anhydride and anhydrous sodium acetate in a reflux apparatus, crystallises in colourless prisms, m. p. 48°, b. p. about 270°, gives a green coloration with ferric chloride in alcoholic solution, and in aqueous solution, especially rapidly in presence of alkali,

undergoes oxidation to a hydroxythymoquinone, m. p. about 165°; this oxidation is favoured also by organic bases, such as aniline, which gives a violet-blue coloration. With phenylcarbimide, it yields the crystalline *phenylurethane*, $C_{24}H_{24}O_4N_2$, m. p. 170°.

T. H. P.

Molybdic Acid-Catechol Compounds. R. F. WEINLAND and FRITZ GAISSER (*Zeitsch. anorg. Chem.*, 1919, **108**, 231—247).—It has been found that catechol reacts with molybdates in aqueous solution to form coloured compounds in which an atom of the oxygen of the molybdate molecule has been displaced by the catechol residue ($C_6H_4O_2$). The simplest of these compounds is prepared by mixing solutions of ammonium molybdate and catechol, in the proportion of 1 molecule of the former to from 6 to 12 of the latter, and allowing the solution to evaporate, when large, deep red crystals in the form of four- or six-sided columns with sharp pyramidal ends are obtained. They can be recrystallised from water, methyl, or ethyl alcohol, and in each case have the composition represented by the formula $(NH_4)H[MoO_3(C_6H_4O_2)],\frac{1}{2}H_2O$. The aqueous solution is gradually decolorised by acids, and the compound is also decomposed by alkalis. Corresponding salts of the alkali metals could not be prepared, bnt by the action of pyridine on the ammonium compound two new compounds were obtained, an ammonium pyridine compound, brownish-red needles, easily soluble in water and methyl alcohol, less easily in ethyl alcohol, to which the formula $(NH_4)(C_5H_5NH)[MoO_3(C_6H_4O_2)],\frac{1}{2}H_2O$, is given, and a pyridine salt. The latter can also be prepared by heating an aqueous solution of molybdic anhydride (1 mol.), catechol (1 mol.), and pyridine (2 to 3 mols.). It forms orange-red aggregates of microscopic needles, m. p. 60°, and its composition corresponds with the formula $(C_5H_5N)H_2[MoO_3(C_6H_4O_2)],1{\cdot}5H_2O$. An anhydrous quinoline salt corresponding in composition with the above ammonium pyridine compound, and a tetramethylammonium compound having the formula $NMe_4H[MoO_3(C_6H_4O_2)]$ were also prepared. An anhydrous dipyridine salt was also obtained.

A dipyridine–dicatechol molybdate was obtained from a solution in which one molecular proportion of molybdic acid was heated with two of catechol and five to ten of pyridine. It forms bright red, six-sided tables, and can be recrystallised from methyl alcohol unchanged, but not from water or ethyl alcohol. It has the composition $(C_5H_5NH)_2[MoO_2(C_6H_4O_2)_2]$, m. p. 137°. In presence of more than two molecular proportions of catechol, the last compound crystallises with the excess of catechol in varying quantities. The compounds isolated contained: (1) $C_6H_4(OH)_2,2H_2O$, m. p. 53°; (2) $\frac{1}{2}C_6H_4(OH)_2$, m. p. 142°; (3) $1{\cdot}5C_6H_4(OH)_2,2H_2O$, m. p. 138°.

E. H. R.

***m*-Anisyltellurium Compounds.** KARL LEDERER (*Ber.*, 1919, **52**, [*B*], 1989—1992. Compare A., 1917, i, 134).—Di-*m*-anisyltelluride has been prepared by the action of magnesium *m*-anisyl iodide on tellurium dibromide; it is purified by conversion into the

rystalline dibromide and reduction of the latter with magnesium nethyl iodide.

Di-m-*anisyltelluride*, $Te(C_6H_4\cdot OMe)_2$, is a pale yellow oil, b. p. 47—252°/34—36 mm., which gives rise to the following *di*-m-*nisyltelluronium* compounds in the usual way; *dichloride*, slender, elted needles, m. p. 162—163°; *dibromide*, small, felted needles, n. p. 185—186°; *di-iodide*, minute, golden-yellow needles, m. p. 67—168° (decomp.), after softening at 163°; *oxide*,

$TeO(C_6H_4\cdot OMe)_2$,

morphous powder, which softens at 69° and is completely molten t 90°; *methiodide*, not obtained in the pure condition. It also orms *additive* compounds with the mercuric haloids as follows: *odide*, $Te(C_6H_4\cdot OMe)_2,HgI_2$, yellow needles, m. p. 122—123°, after oftening at 120°; *bromide*, needles, m. p. 114—115° (decomp.), fter softening at 108°; *chloride*, colourless, amorphous powder, which softens at 83° and is completely molten at about 89°.

H. W.

A Simple and Convenient Way to Prepare Aromatic elenium Compounds. A. SCHOELLER (*Ber.*, 1919, **52**, [*B*], 517—1518).—Instead of treating diazotised anilines with alkali elenides or selenocyanates, which involve the use of hydrogen elenide in their preparation, the same results may be obtained with lkali polyselenides. A reagent is best obtained by fusing black elenium with potassium hydroxide and dissolving the product in ce-water. About twice the theoretical quantity is applied to the iazonium compound, 75% of the excess being precipitated during he reaction and the remainder recovered from the mother liquors f the organic selenide by the action of sulphur dioxide.

Benzenediazonium chloride gives an 80% yield of diphenyl elenide, whilst diazotised anthranilic acid gives a mixture of iselenide (85%) and monoselenide (compare Lesser and Weiss, A., 913, i, 1184; 1915, i, 445). J. C. W.

Cholesterol. XXVIII. Transformation of Cholesterol nto Cholanic Acid. A. WINDAUS and K. NEUKIRCHEN (*Ber.*, 919, **52**, [*B*], 1915—1919).—It has often been surmised that cholic cid, $C_{24}H_{40}O_5$, is intimately connected with cholesterol, $C_{27}H_{46}O$, specially as they give similar colour reactions, but a direct proof as necessitated several years of experiment. A clue was first found n the fact that cholesterol yields acetone on oxidation with chromic cid, whereas cholic acid does not, that is, the difference in the arbon content is that of an *iso*propyl group (A., 1918, ii, 22). Cholanic acid, $C_{24}H_{40}O_2$, which has the three hydroxyl groups of holic acid replaced by hydrogen, behaves in the same way (Wieland nd Weil, A., 1912, i, 831). This led the authors to attempt the emoval of the *iso*propyl group from a suitable cholesterol derivtive, and as a substance in which there are no complications left n the nuclear parts of the molecule, they have chosen cholestane, $C_{27}H_{48}$, the product obtained by the chemical reduction of cholesterol.

When cholestane is oxidised by chromic acid in glacial acetic acid it gives an acid which is remarkably like cholanic acid, but on comparing it with a specimen provided by Wieland it proves to be an isomeride after all. The isomerism is akin to that which exists between cholesterol, dihydrocholesterol, and cholestane on the one hand and coprosterol and ψ-cholestane on the other, for when ψ-cholestane is oxidised in the same way the product is the true cholanic acid.

Cholanic acid has m. p. 164° and its ethyl ester crystallises in long needles, m. p. 93—94°; *isocholanic acid* has m. p. 162° (the mixture begins to soften at 150° and is clear at 155°), the *methyl* ester has m. p. 79—80°, and the *ethyl* ester crystallises in leaflets m. p. 79°. J. C. W.

Xanthosterol, a Crystalline Compound from the Bark of Xanthoxylum Budrunga. H. DIETERLE (*Arch. Pharm.*, 1919 **257**, 260—263).—*Xanthosterol*, $C_{23}H_{40}O$, obtained in about 0·25% yield by extracting the bark of *Xanthoxylum Budrunga* with light petroleum, forms slender, white needles, m. p. 213—214°. Its molecule contains a hydroxyl group, and it forms a *benzoyl* derivative $C_{30}H_{44}O_2$, fine needles, m. p. 264—265°; an *ethylcarbonato*-derivative, $C_{23}H_{39}O{\cdot}CO_2Et$, white, nodular crystals, m. p. 175—176°; a *methylcarbonato*-derivative, $C_{23}H_{39}O{\cdot}CO_2Me$, greasy leaflets, m. p 191—193°; and a *bromo*-derivative, $C_{23}H_{39}OBr$, colourless needles m. p. 169—170°.

Its reactions indicate xanthosterol to be an alcohol related to lupeol (compare Likiernik, A., 1891, 551, 1446; Sack and Tollens A., 1904, i, 1011) and to alstol (Sack and Tollens, *loc. cit.*). With concentrated sulphuric acid, it yields a yellow coloration, which changes to brown with a slight green fluorescence on heating. When its chloroform solution is treated with concentrated sulphuric acid the chloroform gradually becomes pale yellow with a green fluorescence and the acid brown; evaporation of this chloroform solution leaves a violet residue. Addition of concentrated sulphuric acid drop by drop, to a solution of xanthosterol in acetic anhydride give a stable, red coloration.

The bark of *Xanthoxylum Budrunga* contains also an alkaloid, to be studied later. T. H. P.

Condensation of Formaldehyde with some Unsaturated Compounds. H. J. PRINS (*Proc. K. Akad. Wetensch. Amsterdam* 1919, **22**, 51—56. Compare A., 1917, i, 685; 1918, i, 261).—The condensation of formaldehyde with styrene, anethole, camphene and cedrene has been studied. The reaction with styrene yield β-phenyltrimethylene glycol (*loc. cit.*), b. p. 176°/13 mm D_4^{19} 1·1161, n_D^{19} 1·54267, and its *methylene ether*, b. p. 128—130° D_4^{19} 1·1111, n_D^{18} 1·53063. Anethole yields the *methylene ether* o *methoxyphenylbutylene glycol*, b. p. 168—170°/13 mm. 1·1197, n_D^{16} 1·53438. On boiling a solution of trioxymethylen tic acid with camphene for three days, *homocamphenol ace*

is produced, an oil, b. p. 124—128°/13 mm., D_4^{19} 1·0013, n_D^{19} 209. A mixture of cedrene with an equivalent quantity of ıaldehyde in 15% sulphuric acid and acetic acid on stirring for e days yields *homocedrenol*, b. p. 168—171°/13 mm., D_4^{19} 1·0270, 1·51826, along with products of considerably higher boiling t.

J. F. S.

anufacture of Synthetic Drugs [Adrenaline]. NANAYOSHI AI (Brit. Pat. 118298).—Equimolecular proportions of nitro-ıane and diacetylprotocatechualdehyde, prepared by the inter-ɔn of protocatechualdehyde and acetyl chloride or acetic anhy-e, are condensed at ordinary temperatures in presence of a :e solution of a weak alkali to diacetoxyphenylnitroethanol, $_3(OAc)_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$. The crystalline product is col-d, washed free from protocatechualdehyde with ether, and .ed with acetic acid and zinc dust in presence of a 35% form-hyde solution containing a molecular equivalent of formalde-, whereby simultaneous reduction and methylation take place the production of diacetoxyphenylmethylaminoethanol, $_3(OAc)_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NHMe$. The zinc is precipitated from eaction mixture as sulphide, and to the filtered solution the isite amount of hydrochloric acid is added to effect hydrolysis to combine with the liberated base. On evaporation at a low erature in a vacuum, crystals of dihydroxyphenylmethylamino-nol hydrochloride (adrenaline hydrochloride) are obtained.

G. F. M.

enzoylation of some Hydroxy- or Amino-aromatic ıpounds. FRÉDÉRIC REVERDIN (*Helv. Chim. Acta*, 1919, **2**, —The author has recently succeeded in effecting certain diffi-benzoylations by benzoyl chloride in the presence of a little ntrated sulphuric acid (A., 1918, i, 536); the latter substance een employed previously for benzoylation with benzoic anhy-.

H. W.

anufacture of β-Halogen-ethylaminobenzoic Acid Esters. ÉTÉ CHIMIQUE DES USINES DU RHONE (Brit. Pat. 128553).— logen-ethyl-*p*-aminobenzoic esters of the general formula $_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2R$, where X is a halogen and R an alkyl ɔ, are obtained by treating the corresponding hydroxyethyl ounds (Brit. Pat. 128552) with halogenating agents, such as phorus or sulphur haloids, thionyl chloride, or bromide, etc., rably in the presence of a diluent such as benzene or a tertiary e. *Ethyl β-chloroethyl-p-aminobenzoate* is a crystalline sub-e, melting at 69°, and boiling at 183° at 3 mm. pressure. also *J. Soc. Chem. Ind.*, 1920, 43A.]

G. F. M.

anufacture of β-Alkylaminoethylaminobenzoic Alkyl rs. SOCIÉTÉ CHIMIQUE DES USINES DU RHONE (Brit. Pat. 54).—β-Alkylaminoethyl-*p*-aminobenzoic esters are obtained by ng for several hours in a closed vessel at a temperature of

about 100° a mixture of an alkylamine and a β-halogenethyl-aminobenzoic ester (see preceding abstract). *Ethyl β-diethylamin ethylaminobenzoate*, $NEt_2\cdot CH_2\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2Et$, prepared th from diethylamine and ethyl β-chloroethyl-*p*-aminobenzoate, is a oil giving a water-soluble *monohydrochloride* when evaporated dryness with the requisite quantity of dilute hydrochloric acid. C recrystallisation from alcohol the hydrochloride gives white needl melting at 156°. G. F. M.

Manufacture of Substituted Benzoic Acid Ester SOCIÉTÉ CHIMIQUE DES USINES DU RHONE (Brit. Pat. 128912).—I β-halogen-ethyl-*p*-aminobenzoic acid esters of the general formu $N(CH_2\cdot CH_2X)_2\cdot C_6H_4\cdot CO_2R$, where X is a halogen and R an alk group, are prepared in the same way as the monohalogen este (see Brit. Pat. 128553, preceding page), starting from the di-hydroxyethylaminobenzoic esters (see Brit. Pat. 128552). *Eth di-β-chloroethyl-*p*-aminobenzoate* melts at 53° and boils at 215° 3 mm. with slight decomposition. By the method described in Br Pat. 128554 (preceding abstract) the dichloro-esters may be co verted into di-β-alkylaminoethyl-*p*-aminobenzoic esters. Th diethylamine and ethyl di-β-chloroethylaminobenzoate give *eth tetraethyldiaminodiethyl-p-aminobenzoate*,

$$N(CH_2\cdot CH_2\cdot NEt_2)_2\cdot C_6H_4\cdot CO_2Et,$$

which forms a crystalline mass, soluble in dilute hydrochloric ac to give a dihydrochloride; this on crystallisation from alcoh forms white needles, m. p. 194—195°. G. F. M.

Some Derivatives of *p*-Dimethylaminobenzoic Acid.] RIVIER and CH. SCHNEIDER (*Helv. Chim. Acta*, 1919, **2**, 717—71! —*Ethyl* p-*dimethylaminobenzoate* crystallises in colourless leafle m. p. 67—68°. *p*-Dimethylaminobenzanilide has m. p. 181—18 (compare Staudinger and Endle, A., 1917, i, 646), and is convert by phosphorus pentachloride into the *hydrochloride* of p-*dimeth aminobenzanilide iminochloride*, $NPh:CCl\cdot C_6H_4\cdot NMe_2,HCl$. p-*I methylaminothiobenzanilide*, from the anilide and phosphor pentasulphide, forms yellow needles, m. p. 170—171°. H. W.

The Replacement of Halogen attached to a Ring Carb Atom by other Substituents. I. Replacement of Halog by the Carboxyl Group. KARL W. ROSENMUND and ERI STRUCK (*Ber.*, 1919, **52**, [*B*], 1749—1756).—Halogen atoms in ar matic compounds can be directly replaced by carboxyl groups l heating the compounds with aqueous or aqueous-alcoholic pota ium cyanide and a little cuprous cyanide for some hours at abo 200° in strong, sealed tubes. Good results have been obtained wi halogen derivatives of benzene (mono- and di-), toluene, anilir nitrobenzene, phenol, carboxylic acids, naphthalene, and thiophe Apparently, copper is the unique catalyst in such condensations, f in the well-known and easier case of the replacement of halogen the amino-group, silver, nickel, cobalt, zinc, and cadmium salts a almost ineffective.

The following examples are given. Benzoic acid from bromobenzene, p-toluic acid from p-bromotoluene, p-aminobenzoic acid from p-bromoaniline, terephthalic acid from p-dibromobenzene, anisic acid from p-bromoanisole, the three phthalic acids from the three bromobenzoic acids, α-naphthoic acid from α-bromonaphthalene, thiophen-2-carboxylic acid from 2-bromothiophen, and o-3:4-dimethoxybenzoylbenzoic acid, $C_6H_3(OMe)_2\cdot CO\cdot C_6H_4\cdot CO_2H$, small needles, m. p. 208—209°, from *2-bromo-3′:4′-dimethoxybenzophenone* (*o-bromobenzoylveratrole*), stout plates, m. p. 154—155°, this being obtained by the Friedel and Crafts's reaction.

The behaviour of chloronitrobenzenes towards potassium cyanide was investigated by Richter (1871–1873), who found that the meta- and para-compounds gave chlorobenzoic acids when heated with the cyanide solutions at 200° whereas *o*-chloronitrobenzene was unaffected. It is now found that the last isomeride yields *o*-nitrobenzoic acid if a little cuprous cyanide is present and the temperature is not allowed to rise above 195°, whereas at about 210° *phthalic acid and another substance, free from nitrogen and* chlorine, are the products. J. C. W.

Preparation of Tyrosine for the Tyrosinase Reaction. M. W. BEIJERINCK (*Chem. Weekblad*, 1919, **16**, 1494—1495).—A small quantity of trypsinum activum is added to a 10% solution of pepton siccum, the mixture being put in a stoppered flask and shaken with a little chloroform to prevent decomposition by anaërobe bacteria. The flask is kept in a thermostat at 40°, with occasional agitation. After ten to fourteen days the peptone will be converted into tyrosine. *Euphorbia lathyris, Beta vulgaris, Morus nigra*, and *Microspira tyrosinatica* are recommended as sources of tyrosinase. W. J. W.

Intra- and Inter-molecular Active Forces and their Significance in Atomic Rearrangements, in Racemisation, and in Asymmetric Synthesis. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1919, **97**, 198—245).—On reducing active phenylbromolactic acid with zinc in hot alcoholic solution one half of it passes into phenyl-β-lactic acid and the other half into cinnamic acid. When the zinc salts of the acids are decomposed with dilute sulphuric acid and the cinnamic acid is extracted with ether, it is found to be optically active, rotating in the same direction as the active phenylbromolactic acid from which it is derived. That this activity of the cinnamic acid is not due to contamination with phenyl-lactic acid is shown by experiments in which repeated extractions with water still leave an active cinnamic acid. This is further confirmed by the fact that a mixture of *i*-cinnamic acid with active phenyl-lactic acid of the same optical activity as that shown by the active cinnamic acid differs from it in other respects. The active cinnamic acid obtained as above shows *an asymmetric crystalline form*. On brominating a mixture of the zinc salts of *d*-phenyl-lactic acid and *i*-cinnamic acid the *l*-dibromide of cinnamic acid is obtained. On the other hand, *l*-phenyl-lactic acid and *i*-cinnamic

acid yield the *d*-dibromide. The reduction products of *l*- and phenylbromolactic acids, likewise, yield dibromides of cinnamic ac of the opposite rotation to the phenylbromolactic acids employe Further experiments with *d*-tartaric acid, *l*-chlorosuccinic aci *l*-mandelic acid, and *i*-cinnamic acid have shown the following:—

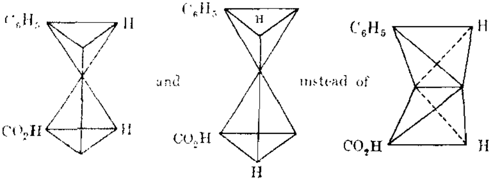
i-Cinnamic acid with *d*-tartaric acid yields *l*-cinnamic acid + $Br_2 \longrightarrow$ *d*-dibromide.

i-Cinnamic acid with *l*-chlorosuccinic acid yields *d*-cinnami acid + $Br_2 \longrightarrow$ *l*-dibromide.

i-Cinnamic acid with *l*-mandelic acid yields *d*-cinnamic acid + $Br_2 \longrightarrow$ *l*-dibromide.

On treating *d*-cinchonine with *i*-cinnamic acid, *l*-cinnamic acid i obtained, and on bromination the *d*-dibromide is formed.

As the geometrical isomeric formula of cinnamic acid with th double bond cannot account for the active cinnamic acids, th author suggests a stereoisomeric structure with free unsaturate affinities thus:



He also suggests that the activation of the cinnamic acid in the above reactions is brought about by the "induction" influence of the asymmetric active components involved in the reactions, namely, the phenyl-lactic acids, *d*-tartaric acid, *l*-chlorosuccinic acid, etc.

The stereoisomerism of the optically active *iso*valeric acid obtained by the author and Landsherger from the brucine salt of methylethylmalonic acid is also discussed. S. S. Z.

The Explanation of the Reciprocal Action of Asymmetric Substances with an Asymmetric Carbon Atom on Cinnamic and *allo*-Cinnamic Acids as Based on the Author's Isomerism Theory of the Ethylene Derivatives. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1919, **97**, 245—255).—Applying the theory advanced in the preceding paper, the author discusses the action of some asymmetric substances on cinnamic and *allo*-cinnamic acids. The stereoisomeric formulæ of storax-α-cinnamic acid, storax-β-cinnamic acid, triclinic cinnamic acid, *allo*cinnamic acid, *iso*cinnamic acid (Liebermann), and *iso*cinnamic acid (Erlenmeyer, sen.) are discussed. S. S. Z.

Walden's Inversion. EMIL ERLENMEYER (*Biochem. Zeitsch* 1919, **97**, 255—261).—A theoretical paper. Walden's inversic is discussed in the light of the author's "induction" theo described in the preceding abstracts. S. S. Z.

Concerning the Force Emanating from Asymmetri Molecules and its Significance in Biochemistry. EMI ERLENMEYER (*Biochem. Zeitsch.*, 1919, **97**, 261—311).—. theoretical paper. A lengthy exposition of the author's theory a to the stereoisomerism of ethylene derivatives and the "induction influence of asymmetric active compounds (see preceding abstracts Many observations already made in stereochemistry and bi chemistry are discussed in the light of the new hypotheses.

S. S. Z.

Compounds of Molybdic Acid with Aromatic *o*-Hydr oxy-Acids (Salicylic Acid and α-Hydroxynaphthoic Acid R. F. WEINLAND and KURT ZIMMERMANN (*Zeitsch. anorg. Chem* 1919, **108**, 248—266).—It has been found that salicylic acid an α-hydroxynaphthoic acid combine with molybdic acid to form series of coloured complex compounds. The complex acids then selves could not be isolated, but a number of pyridine, quinolin and tetramethylammonium salts were prepared in crystalline co dition. No compounds are formed between molybdic acid and *m* or *p*-hydroxybenzoic acids. The evideuce indicates that onl the hydroxy-group of the organic acid interacts with the molybd acid, not the carboxyl group.

By heating together in aqueous solution molybdic anhydrid salicylic acid, and *pyridine* in the *molecular* proportions 1 : 7 : 7, deep yellow salt crystallising in thick, irregular, six-sided tabl was obtained having the composition

$$4[MoO_2(O{\cdot}C_6H_4{\cdot}CO_2)_2]H_2,9C_5H_5N,4H_2O$$

(No. 1). When prepared in methyl-alcoholic solution, the same sa was obtained anhydrous. It cannot be recrystallised unchange Quinoline and tetramethylammonium salts of the same comple acid were prepared, and were all yellow. The correspondin pyridine salt containing α-hydroxynaphthoic acid is yellow. Th is a complex acid salt containing 15 molecules of hydroxynaphtho acid to 7 of molybdic acid and 13 of pyridine (No. 5). When th is heated with methyl alcohol, it is changed into the normal sal $MoO_2(O{\cdot}C_{10}H_6{\cdot}CO_2)_2(H{\cdot}C_5H_5N)_2,5H_2O$ (No. 6). When the con pound No. 1 is heated with methyl alcohol, a new compoun crystallises which has the composition

$$6[C_7H_4O_2(Mo_2O_7)]H_2,7C_5H_5N,3CH_3{\cdot}OH$$

(No. 11). This compound contains the new acid,

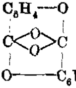
$$[C_6H_4(CO_2)Mo_2O_7]H_2.$$

The same anion appears to be present in a flesh-red compoun which is formed by heating the pyridine salt No. 1 with water, an has the formula $8[C_7H_4O_2(Mo_2O_7)]H_2,9C_5H_5N$ (No. 10). A simila flesh-coloured salt is obtained when No. 11 is heated in water; th has the composition $[C_7H_4O_2(MoO_3)_2]C_5H_5N,H_2O$ (No. 12). B

heating the salt No. 5 with water, a yellowish-grey compound is obtained having the composition $[C_{11}H_6O_2(MoO_3)_2],C_5H_5N$ (No. 13).

Sodium, potassium, and ammonium salts of salicylomolybdic acid were also prepared. These were brownish-red compounds of very complex constitution, and appear to be double salts of mono-salicylomolybdic acid, $[MoO_3{\cdot}O{\cdot}C_6H_4{\cdot}CO_2]H_2$, and disalicylomolybdic acid, $[MoO_2(O{\cdot}C_6H_4{\cdot}CO_2)_2]H_2$. E. H. R.

A New Disalicylide. RICHARD ANSCHÜTZ [with HANS JANSEN, ALFRED LUBLIN, and GEORG METZGES] (*Ber.*, 1919, **52**, [*B*], 1875—1895).—By the distillation of *o*-acetoxybenzoic acid under less than 20 mm. pressure, the author has obtained Einhorn and Pfeiffer's disalicylide, m. p. 200° (A., 1901, i, 712), and a new isomeride, m. p. 213°, which is less soluble in chloroform than the old one. It is found that the new isomeride, designated *α-disalicylide* (small, glistening prisms, m. p. 213°), is the normal disalicylide of the formula $C_6H_4{<}^{O\cdot CO}_{CO\cdot O}{>}C_6H_4$, whereas the older, *β-disalicylide*, is probably represented by the annexed formula.



When distilled under reduced pressure, each passes to a slight extent into the other, but under atmospheric pressure they both give xanthone and carbon dioxide. Several other salicylic acid derivatives give the same pair of disalicylides when carefully distilled under reduced pressure, namely, tetrasalicylide, polysalicylide, diplosal (salicoylsalicylic acid), acetyldiplosal (*o*-2-acetoxybenzoyloxybenzoic acid, D.R.-P. 236196), and 2:2′-diacetoxybenzoic anhydride (from aspirin, by the action of thionyl chloride and pyridine, D.R.-P. 201329).

The α-disalicylide reacts with boiling alcohols to give the esters of diplosal; *methyl o-2-hydroxybenzoyloxybenzoate* (*methyl salicoylsalicylate*), $OH{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2Me$, has m. p. 86—87°, and the *ethyl* ester, m. p. 59°, agreeing with specimens made by the action of alcoholic hydrogen chloride on diplosal. The β-disalicylide is much more stable towards alcohols. When heated with methyl alcohol at 150° for six hours, it is partly converted into methyl salicylate. Similarly, the α-isomeride reacts with ammonia in chloroform solution about five times as fast as the β-form, giving the *ammonium disalicoylimide*,

$$(HO{\cdot}C_6H_4{\cdot}CO)_2N{\cdot}NH_4.$$

This is a canary-yellow powder which may be obtained from methyl salicylate, through the amide and imide (Schulerud, A., 1881, 42). The ammonium salt has been converted into the following salts: *silver*, $(HO{\cdot}C_6H_4{\cdot}CO)_2N{\cdot}Ag$; *calcium*, $CaX_2,2H_2O$; *strontium*, $SrX_2,3H_2O$; *barium*, BaX_2,H_2O; *mercuric*, HgX; *cupric*, CuX; and *lead*, PbX. α-Disalicylide also reacts with aniline and *p*-toluidine at about 100°, giving *disalicoylanilide*,

$$NPh(CO{\cdot}C_6H_4{\cdot}OH)_2,$$

m. p. 165°, and *disalicoyl-p-toluidide*, m. p. 149°. J. C. W.

Isomerism of [Methyl] *o*-Benzoylbenzoate. A. HANTZSCH (*Ber.*, 1919, **52**, [*B*], 1572—1573).—McMullen (A., 1916, i, 560) doubted the existence of isomerism in the case of methyl *o*-benzoylbenzoate because he could not obtain the ψ-form described by Meyer (A., 1904, i, 747). Hantzsch points out that he was successful in isolating this isomeride (A., 1916, i, 399). J. C. W.

Oxidative Degradation of Dehydro*iso*fenchoic Acid [Dehydro*iso*fenchocamphoric Acid]. N. J. TOIVONEN (*Annalen*, 1919, **419**, 176—216).—The experiments were originally undertaken with the object of elucidating the composition of dehydro*iso*fenchoic acid; meanwhile, this has been accomplished by other methods (compare Aschan, A., 1913, i, 198), and the paper mainly gives an account of an instance of abnormal oxidation by permanganate in alkaline solution.

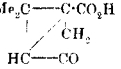
dl-Dehydro*iso*fenchoic acid was prepared by the successive action of phosphorus pentachloride and bromine on *dl*-*iso*fenchoic acid, conversion of the product into the ethyl ester, removal of hydrogen bromide from the latter by means of quinoline, and subsequent hydrolysis; it has m. p. 190—191°, and is soluble in water at 25° to the extent of 0·1061 gram in 100 grams. The ethyl ester has b. p. 131—134°/9—10 mm., 260—262°/772 mm., D_4^{20} 1·0121, n_D^{20} 1·45738. The monoethyl ester (β-form?) is a colourless, viscous liquid, b. p. 168—171°/9 mm., D_4^{20} 1·0730, whilst a second *modification* (α-form?) has b. p. 178—180°/15 mm., m. p. 50—51°, D_4^{20} 1·0737, n_D^{22} 1·47232. Attempts to convert the acid into an anhydride by means of acetyl chloride were unsuccessful, and it was not isomerised by a mixture of glacial acetic and hydrochloric acids (D 1·2). It did not unite with bromine. Hydrogen bromide, on the other hand, readily combined with it, yielding an *acid*, $C_{10}H_{15}O_4Br$, m. p. 267° (decomp.), which was not dehydrated by acetyl chloride, and, on energetic reduction, gave *r*-*cis*-*iso*-fenchoic acid. (The investigation of this action is not yet completed.) d-*Dehydro*iso*fenchoic acid*, prepared similarly to the *dl*-*acid*, *forms monoclinic needles and leaflets, m. p.* 170—171°, $[\alpha]_D^{17.5}$ +30·28° in alcoholic solution, and is soluble in water to the extent of 0·3761 gram in 100 grams at 25°. The *diethyl* ester is a colourless, mobile liquid, b. p. 123°/6 mm., 261—262°/772 mm., D_4^{20} 1·0130, n_D^{21} 1·45892, $[\alpha]_D^{23}$ +36·69°. The *monoethyl* ester (β-form?) has b. p. 164°/8 mm., D_4^{20} 1·0760, n_D^{21} 1·46931, $[\alpha]_D^{20}$ +40·26°, *whilst the corresponding α-variety* (?) has b. p. 169—170°/8 mm., m. p. 46—47°, $[\alpha]_D^{19}$ +19·71° in alcoholic solution. l-*Dehydro*iso*fenchoic acid* has m. p. 170—171°, $[\alpha]_D^{20}$ −30·43° *in alcohol, and dissolves in water to the extent of* 0·3735 *gram in* 100 *grams at* 25° (*diethyl* ester, colourless, mobile liquid, b. p. 140—143°/10 mm., 262—263°/772 mm., D_4^{20} 1·0145, n_D^{19} 1·45709, $[\alpha]_D^{19}$ −36·18°; *monoethyl* ester, [β-form], colourless, almost odourless, viscous liquid, b. p. 172—175°/10 mm.).

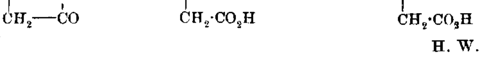
When a faintly alkaline solution of dehydro*iso*fenchoic acid is oxidised by potassium permanganate (1%) at 0°, about two atoms

of oxygen are absorbed, and the syrupy product appears to consist mainly of a *lactonic acid*, which could not be isolated in the pure condition. At ordinary temperatures under the same conditions, oxidation proceeds until rather more than four atoms of oxygen have been used, and the product is a crystalline acid, $C_8H_{10}O_3$ (see later). If, however, a brisk current of carbon dioxide is passed through the mixture during oxidation and an excess of acid is immediately added, *αδ-diketo-ββ-dimethylhexoic acid*,

$CO_2H·CO·CMe_2·CH_2·COMe$,

is obtained as a colourless, viscous liquid, which can be neither caused to crystallise nor distilled, even under diminished pressure. It does not appear to react normally with phenylhydrazine or semicarbazide, but its constitution follows from its oxidation by hydrogen peroxide to mesitonic acid, $CO_2H·CMe_2·CH_2·COMe$, m. p. 75° (*semicarbazone*, m. p. 197·5° [decomp.], phenylhydrazone, m. p. 135°). The acid is converted by boiling dilute solutions of alkali hydroxides into the acid, $C_8H_{10}O_3$, which is identical with the substance described by Perkin, Thorpe, and Walker (T., 1901, **79**, 729), to which they ascribed the annexed formula. It has m. p. 180° (*semicarbazone*, m. p. 255°, phenylhydrazone, yellow needles, m. p. 222°, *methyl* ester, colourless, moderately mobile liquid, b. p. 112—113°/14 mm., D_4^{20} 1·0783, $n_D^{15·5}$ 1·47860). It is converted by bromine in acetic acid solution into a *dibromo-acid*, $C_8H_{10}O_3Br_2$, shining, rhombic leaflets, m. p. 164°, which, on reduction with zinc dust and acetic acid, yields dimethyl*cyclo*pentanonecarboxylic acid, m. p. 104°, which is also obtained by reduction of the acid, $C_8H_{10}O_3$, itself (compare Perkin, Walker, and Thorpe, *loc. cit.*). When oxidised by permanganate in alkaline solution, it yields *αα-dihydroxy-ββ-dimethylglutaric acid*, m. p. 85° (which, when preserved in a vacuum desiccator, readily passes into *α-keto-ββ-dimethylglutaric acid*, m. p. 99°), and *as*-dimethylsuccinic acid. The author doubts the correctness of the formula ascribed to the acid, $C_8H_{10}O_3$, by Perkin, Walker, and Thorpe, and prefers to regard it as 5:5-dimethyl-Δ^1-*cyclo*penten-3-one-1-carboxylic acid, its oxidation occurring in accordance with the scheme:





H. W.

The Derivation of Valency Laws. The Principle of and Cationic Partial Valencies. HUGO KAUFFMANN (*Ber.*, 1919, **52** p-tolul, 1422—1435).—In connexion with the problem of halochromit has already been shown that the basic functions of the dye m. p. 16the colour of its salts do not always run parallel. In the case dimethoxy-derivatives of triphenylcarbinol, for example, it

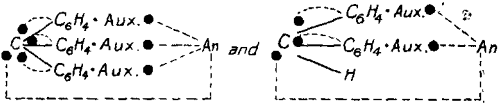
has been found that whereas the 2:4-compounds are more basic than the 3:4-, and these much more so than the 2:5-isomerides, the latter give the deepest coloured salts. That is, resorcinol derivatives give the strongest bases, but quinol derivatives the most deeply coloured salts (A., 1914, i, 39). The principle may be established, therefore, that two auxochromes have the greatest effect on a *chromogen when they are in the para-position to each other.* This principle has already been tested in the case of benzene derivatives having the auxochrome and chromophore in the same ring (A., 1906, i, 841; 1911, i, 368, 930; 1912, i, 863), but now, in order to throw light on the triphenylcarbinol salts, it has been examined in the case of some compounds in which the chromophore is connected by a carbon chain to the nucleus. The methoxyl group is *chosen as the auxochrome, to avoid complications such as quinonoid* isomerism and betaine-like salt formation. As the following table shows, the 2:5-isomerides have the deepest shades of colour.

Chromophore.	2 : 5-.	3 : 4-.	2 : 4-.
$CH:CH\cdot NO_2$	Orange-red	Yellow	Yellow
$CH:CMe\cdot NO_2$	Orange	Pale yellow	Yellow
$CH:CPh\cdot NO_2$	Orange	Lemon-yellow	Yellow
$CH:CPh\cdot CO_2H$	Pale yellow	White	White
$CH:CPh\cdot CN$	Yellow	White	Pale yellow
$CH:C(CN)\cdot CO_2Et$......	Yellow or orange	White	Greenish-yellow
$CH:C(CN)\cdot CN$	Golden-yellow	Pale yellow	Pale yellow
$CH:CBz\cdot CN$	Yellow or orange	Straw-yellow	Pale yellow
$CH:C<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4$ ...	Brick-red	Chrome-yellow	Lemon-yellow

It follows, therefore, that the salt character of a triphenylcarbinol derivative is governed by one law and its colour by another, *quite independent in its operation, and, consequently, a formula* for these dyes must be so adduced that it is possible to express in it how variations in colour and salt character can proceed independently. None of the formulæ proposed hitherto satisfy this condition, not even Hantzsch's "conjugation" formula (A., 1919, ii, 254). The author proceeds to develop an electrochemical hypothesis, from the two principles already laid down by him, namely, the law of the decentralisation of chemical functions (A., 1914, i, 40) and the principle of variable states (A., 1916, i, 417).

The valency of a system which is directed towards an anion is *termed a "cation valency."* This may have its seat in one atom of the system, but is generally divided and the partial valencies distributed over several parts of the molecule. The more the valency is subdivided, the more strongly basic will the system be. Subdivision of valencies is also the cause of colour, and auxochromes are groups which provide cationic partial valencies. In the case of the triphenylmethane compounds, any change in the cationic valency fragments of the auxochrome is accompanied by a similar change at the central carbon atom. That is, the more the auxochrome valency is subdivided the more also will the fourth *valency of the central carbon atom be, and these valency fragments* will be cationic, for they are opposed to the auxochrome valencies.

In the case of crystal-violet and tetramethyldiaminobenzhydrol the "formulæ of state" may be written thus:



where Aux. = auxochrome, an. = anion, and the heavy points mark the seat of cationic partial valencies. In the first compound the auxochrome and central carbon atom valencies are more scattered than in the second, and it is therefore more basic. It is not much more deeply coloured, however, from which it follows that subdivision of cationic valencies does not cause colour, and the central carbon atom in the triphenylmethane dyes is not the seat of the colour. These dyes have three seats of colour, namely, the ring carbon atoms, which are united to the central carbon atom.

The following new compounds are prepared by the condensation of the dimethoxybenzaldehydes with various agents. *ω-Nitro-3:4-dimethoxy-ω-methylstyrene*, $C_6H_3(OMe)_2$·CH:CMe·NO_2, m. p. 73°, and the 2:4-*dimethoxy*-compound, m. p. 79°, from nitroethane under the influence of ethylamine. *β-Nitro-3:4-dimethoxystilbene*, $C_6H_3(OMe)_2$·CH:CPh·NO_2, m. p. 109°, and the 2:4-*dimethoxy*-compound, m. p. 120°, from phenylnitromethane. 3:4-*Dimethoxy-α-phenylcinnamic acid*, $C_6H_3(OMe)_2$·CH:CPh·CO_2H, m. p. 224°, and the 2:4-*dimethoxy*-compound, slender needles, m. p. 191°, from sodium phenylacetate and acetic anhydride. *Ethyl α-cyano-3:4-dimethoxycinnamate*, $C_6H_3(OMe)_2$·CH:C(CN)·CO_2Et, m. p. 155°, and the 2:4-*dimethoxy*-compound, m. p. 143°, from ethyl cyanoacetate. *α-Cyano-3:4-dimethoxycinnamonitrile*,

$C_6H_3(OMe)_2$·CH:C$(CN)_2$,

m. p. 147°, and the 2:4-*dimethoxy*-compound, m. p. 144°, from malononitrile. *Phenyl α-cyano-3:4-dimethoxystyryl ketone*, $C_6H_3(OMe)_2$·CH:CBz·CN, slender needles, m. p. 106°, and the 2:4-*dimethoxy*-compound, m. p. 156°, from ω-cyanoacetophenone. *Phenyl α-cyano-3:4-methylenedioxystyryl ketone*, lemon-yellow needles, m. p. 138°, from piperonaldehyde and ω-cyanoacetophenone, and *phenyl α-cyano-4-hydroxy-3-methoxystyryl ketone*, deep yellow crystals, m. p. 143°, from vanillin. J. C. W.

Resolution of Acid Salts of Dibasic Acids [into Normal Salts and Free Acids] in Aqueous Solution. IV. TH. SABALITSCHKA (*Ber.*, 1919, **52**, [*B*], 1776. Compare A., 1917, i, 700; 1919, ii, 282, i, 433).—Phthalic acid is not dehydrated if its ethereal solution is evaporated without a catalyst, but a trace of sulphuric acid is sufficient to cause the production of considerable quantities of the anhydride (compare Dieckmann and Hardt, A., 1919, ii, 326). After extracting a solution of normal potassium phthalate (0·54

gram in 30 c.c.) for twenty hours with ether, the extract was found to require about 1 c.c. of 0·01*N*-potassium hydroxide for neutralisation, and the aqueous solution the same amount of acid.

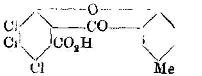
J. C. W.

Condensation of Phthalic Anhydride with Phenols in the Presence of Aluminium Chloride. Fritz Ullmann and Walter Schmidt (*Ber.*, 1919, **52**, [*B*], 2098–2118).—Phenols may be condensed with phthalic anhydride by means of aluminium chloride if acetylene tetrachloride is used as solvent, hydroxybenzoylbenzoic acid derivatives being formed in uniformly good yield. The carbonyl group of the phthalic anhydride attaches itself for the most part to the carbon atom in the *ortho*-position to the hydroxyl group of the phenol. Starting from tetrachlorophthalic anhydride, *o*-hydroxybenzoylbenzoic acid derivatives are almost exclusively obtained, which are readily converted by alkalis into xanthone derivatives.

Phthalic anhydride and *p*-cresol yield *4-hydroxy-*m*-toluoyl-*o*-benzoic acid*, $OH{\cdot}C_6H_3Me{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, colourless, prismatic crystals, m. p. 194—195° (corr.), which is converted by sulphuric acid into 1-hydroxy-4-methylanthraquinone, reddish-yellow needles, m. p. 175° (corr.). 3-Hydroxy-*p*-toluoyl-*o*-benzoic acid, prisms, m. p. 211—212° (corr.), and *5-hydroxy-*o*-toluoyl-*o*-benzoic acid*, colourless, rhombic leaflets, m. p. 219—220°, are similarly obtained from *m*-cresol, and are best separated by fractional crystallisation from nitrobenzene. In the same manner, *o*-cresol gives a mixture of 2-hydroxy-*m*-toluoyl-*o*-benzoic acid, prisms, m. p. 196—197° (corr.), and *6-hydroxy-*m*-toluoyl-*o*-benzoic acid*, colourless, rhombic leaflets, m. p. 224—226° (corr.). *2'-Hydroxy-*o*-benzoylbenzoic acid*, prismatic crystals, m. p. 171—172° (corr.), *4'-hydroxy-*o*-benzoylbenzoic acid*, rhombic leaflets, m. p. 210° (identified by comparison with the acid obtained by the fission of phenolphthaleinoxime), and small amounts of phenolphthalein are obtained from phenol. *6-Chloro-3-hydroxy-*p*-toluoyl-*o*-benzoic acid*, colourless prisms, m. p. 205—206° (corr.), is prepared from *p*-chloro-*m*-cresol, and is transformed by sulphuric acid monohydrate into *4-chloro-1-hydroxy-3-methylanthraquinone*, orange-red needles, m. p. 177° (corr.). The latter is converted by *p*-toluidine in the presence of copper powder into *1-hydroxy-4-*p*-toluidino-3-methylanthraquinone*, bluish-violet needles, m. p. 191° (corr.); the chlorine atom can be replaced by the hydroxyl group by treatment with sulphuric and boric acids at 150—160°, whereby 1 : 4-dihydroxy-2-methylanthraquinone (2-methylquinizarin), carmine-red needles, m. p. 177° (corr.), is formed. It is transformed by nitrous acid in the presence of boric and sulphuric acids into quinizarin-2-carboxylic acid, carmine-red, matted needles, m. p. 249—250° (corr.). *1-Hydroxy-4-toluenesulphonamido-3-methylanthraquinone*, yellowish-brown needles, m. p. 213—214° (corr.), is obtained by heating the chlorohydroxymethylanthraquinone with potassium acetate, *p*-toluenesulphonamide, and

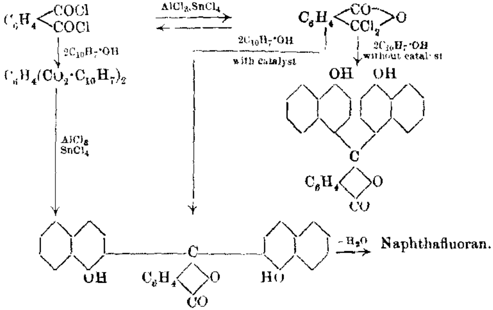
copper acetate in amyl-alcoholic solution, and is hydrolysed to 4-*amino*-1-*hydroxy*-3-*methylanthraquinone*, violet needles, m. p. 257—258° (corr.). When heated with potassium and copper acetates in the presence of naphthalene, the chlorohydroxymethylanthraquinone yields 1-hydroxy-3-methylanthraquinone, m. p. 178° (corr.).

The condensation of *p*-cresol with tetrachlorophthalic anhydride gives 3:4:5:6-*tetrachloro*-4′-*hydroxy*-m-*toluoyl*-o-*benzoic acid*, m. p. 232—235° (corr.), according to the rate of heating, which is quantitatively transformed by alkali carbonate or hydroxide into 5:6:7-*trichloro*-2-*methylxanthone*-8-*carboxylic acid* (annexed formula), colourless, prismatic needles, m. p. 263—266° (corr.). Under similar conditions, *m*-cresol gives 3:4:5:6-*tetrachloro*-3′-*hydroxy*-p-*toluoyl*-o-*benzoic acid*, pale yellow, prismatic plates, m. p. 226—228° (corr.), which yields 5:6:7-*trichloro*-3-*methylxanthone*-8-*carboxylic acid*, long, colourless, prismatic needles, m. p. 254—256° (corr., decomp.). 3:4:5:6-*Tetrachloro*-2′-*hydroxy*-m-*toluoyl*-o-*benzoic acid*, yellow, rhombic plates, m. p. 222—225° (corr.), and 5:6:7-*trichloro*-4-*methylxanthone*-8-*carboxylic acid*, colourless, prismatic needles, m. p. 270—273° (decomp.), are successively prepared from *o*-cresol. Phenol yields 3:4:5:6-*tetrachloro*-2′-*hydroxy*-o-*benzoylbenzoic acid*, colourless, shining leaflets, m. p. 216—218° (corr.), and 5:6:7-*trichloroxanthone*-8-*carboxylic acid*, colourless, prismatic needles, m. p. 261—264° (corr.), whilst β-naphthol gives 3:4:5:6-*tetrachloro*-2′-*hydroxy*-2-α-*naphthoylbenzoic acid*, yellow, rhombic plates, m. p. 214—217° (corr.), and 4′:5′:6′-*trichloro*-1:2-*naphthaxanthone*-1′-*carboxylic acid*, needles, m. p. 273—275° (corr, decomp.). H. W.



Condensation of Phthalyl Chloride with α-Naphthol. WILHELM CSÁNYI (*Ber.*, 1919, **52**, [*B*], 1788—1793. Compare Werner, T., 1918, **113**, 20).—The following compounds have been isolated from the product of the condensation of phthalyl chloride with α-naphthol by Sörensen and Palitzsch's method (A., 1910, ii, 446). (1) α-*Naphthyl phthalate*, pale yellow bundles of needles, m. p. 155°, insoluble in sodium hydroxide. (2) An *o*-naphtholphthalein, almost insoluble in cold alcohol, crystallising from the hot solvent in yellowish-red, prismatic needles, m. p. 234—235°; soluble with dark green colour in sodium hydroxide (compare Copisarow and Weizmann, T., 1915, **107**, 878); soluble with ultramarine colour in concentrated sulphuric acid, the solution becoming eosin-red with ochre-yellow fluorescence on warming, owing to dehydration to α-naphthafluoran. (3) The *p*-naphtholphthalein, which dissolves in cold alcohol, gives a blue solution in sodium hydroxide, and cannot be condensed to the fluoran. Under the above conditions the yield of the ortho-phthalein is very small, but it is greatly increased if anhydrous aluminium or stannic chloride is present.

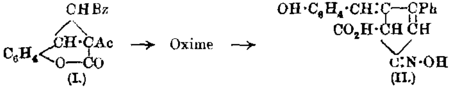
The complete system, a-naphthol–phthalyl chloride, is influenced, therefore, by the tautomerism of phthalyl chloride, the equilibrium of which is displaced in favour of the unsymmetrical form by the metallic chlorides, and also by the effect of these agents on the ester (compare A., 1919, i, 327). The system is reproduced thus:



J. C. W.

A New Group of *cyclo*Propane Derivatives. IV. Derivatives of the 3-Acyl-3 : 4-phenacylidenedihydrocoumarins. OSKAR WIDMAN (*Ber.*, 1919, **52**, [*B*], 1652—1662. Compare A., 1918, i, 347, 398).—Some reactions of 3-acetyl- and 3-propionyl-3 : 4-phenacylidenedihydrocoumarins and phenacylidenecoumarinic esters are described.

3-Acetyl-3 : 4-phenacylidenedihydrocoumarin (I) forms an *oxime*, quadratic prisms or elongated tablets, m. p. 230° (decomp.), which dissolves in dilute sodium hydroxide on boiling, the yellowish-red solution depositing a *compound*, probably of the formula (II), on acidifying. This product crystallises in small, yellow tablets or prisms, m. p. 184° (decomp.). When treated with semicarbazide



(I.) (II.)

hydrochloride in methyl or ethyl alcohol, alcoholates of the semicarbazone are formed. These lose the alcohol at about 115° in a vacuum, giving the pale yellow *semicarbazone*,

$$C_{19}H_{14}O_3{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

m. p. 204° (decomp.); the *compound* with 1EtOH, crystallises in

long needles which change into small rhombohedra, and the *compound* with 1MeOH forms small, quadratic tablets. In acetic acid solution, however, the product is salicylaldehydesemicarbazone. Similarly, hydrazine hydrochloride produces the azine of salicylaldehyde.

When shaken with sodium ethoxide solution, the 3-acetyl derivative gradually deposits the yellow salt of *α-acetyl-αβ-phenacylidene-dihydrocoumaric acid*, $OH\cdot C_6H_4\cdot CH{<}^{CHBz}_{}{>}CAc\cdot CO_2H$ (CHBz bridging CH—CAc). The free acid crystallises in colourless, quadratic pyramids, m. p. 177° (decomp.), and slowly reduces permanganate in acetone. The compound also dissolves in boiling 10% sodium hydroxide, depositing a scarlet, flaky salt on cooling, which evolves carbon dioxide and salicylaldehyde (?) on acidifying, thereby changing into *3-keto-1-phenyl-5-salicylidene-Δ¹-cyclopentene*, $CO{<}{}^{CH_2\cdot C:CH\cdot C_6H_4\cdot OH}_{CH=CPh}$. This crystallises in nodules of yellow needles, m. p. 202°, readily reduces permanganate, and forms an *acetyl* derivative, pale yellow filaments, m. p. 161°, which yields an *oxime*, pale yellow filaments, m. p. 167° (decomp.), and an *azine*, $[C_{20}H_{16}ON]_2N_2$, reddish-brown filaments, m. p. 232°.

Ethyl α-acetyl-αβ-phenacylidenedihydrocoumarinate dissolves in dilute sodium hydroxide on boiling, and on acidifying the solution deposits *2-hydroxy-4-phenyl-5-α-hydroxy-o-ethoxybenzyl-Δ¹,³-cyclopentadiene-1-carboxylic acid*,

$$OH\cdot C{<}{}^{C(CO_2H)\cdot CH\cdot CH(OH)\cdot C_6H_4\cdot OEt}_{CH{=\!=}CPh}.$$

This crystallises in large, pale yellow, quadratic prisms, m. p. 164° (decomp.), gives an intense violet coloration with ferric chloride, and forms a *lactone*, glassy, rhombic tablets, m. p. 137—138°, on boiling with acetic anhydride.

3-Propionyl-3 : 4-phenacylidenedihydrocoumarin reacts with dilute sodium hydroxide to form *3-keto-1-phenyl-5-salicylidene-2-methyl-Δ¹-cyclopentene*, straw-yellow tablets or prisms, m. p. 250°, and ethyl α-propionyl-αβ-phenacylidenedihydrocoumarinate yields 2-*hydroxy-4-phenyl-5-α-hydroxy-o-ethoxybenzyl-3-methyl-Δ¹,³-cyclopentadiene-1-carboxylic acid*, stout prisms, m. p. 138°. J. C. W.

Hydroxy- and Dihydroxy-phenylserines and the Parent Substance of Adrenaline. KARL W. ROSENMUND and H. DORNSAFT (*Ber.*, 1919, **52**, [*B*], 1734—1749).—Erlenmeyer's synthesis of h ayylserines from aromatic aldehydes and glycine (A., 1905, i, 131) oxide, very limited application, but a modification which would e condif the production of phenolic serines would be of considergreatly est, because of the relationship between such compounds sent. line. Three methods have now been tested, the third ful, consisting in the condensation of the aldehydes

with ethyl glycine in the presence of sodium The reaction is represented thus:

(1) $R{\cdot}CHO + NH_2{\cdot}CH_2{\cdot}CO_2Et = R{\cdot}CH{:}N{\cdot}CH_2{\cdot}CO_2Et + H_2O$;
(2) $R{\cdot}CHO + R{\cdot}CH{:}N{\cdot}CH_2{\cdot}CO_2Et =$
$R{\cdot}CH(OH){\cdot}CH(CO_2Et){\cdot}N{:}CHR$

(that is, aldol condensation); (3) hydrolysis to
$R{\cdot}CH(OH){\cdot}CH(NH_2){\cdot}CO_2H + R{\cdot}CHO$.
In the case of phenolic aldehydes, the hydroxy-groups are protected by transforming them into ethylcarbonato-groups, which are subsequently removed by treatment with dilute sodium hydroxide in an atmosphere of hydrogen (Fischer's method).

Various views on the development of adrenaline in the body are criticised, and the following scheme is suggested, the precursor being the 3:4-dihydroxyphenylalanine of proteins (Guggenheim, A., 1914, i, 49): ($R = C_6H_3[OH]_2$)

$$R{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H \longrightarrow R{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow$$
$$R{\cdot}CH_2{\cdot}CO_2H \longrightarrow R{\cdot}CO{\cdot}CO_2H$$
$$R{\cdot}CO{\cdot}CO_2H + NH_2{\cdot}CH_2{\cdot}CO_2H - CO_2 \longrightarrow$$
$$R{\cdot}CH(OH){\cdot}CH(NH_2){\cdot}CO_2H \longrightarrow R{\cdot}CH(OH){\cdot}CH(NHMe){\cdot}CO_2H \longrightarrow$$
$$R{\cdot}CH(OH){\cdot}CH_2{\cdot}NHMe.$$

It is quite possible that the 3:4-dihydroxyphenylserine itself is a hydrolytic product of protein.

The Unsuccessful Attempts.—Anisaldehyde and ethyl chloroacetate, condensed together by Claisen's method (A., 1905, i, 286), yield *ethyl* p-*methoxyphenylglycidate*, $OMe{\cdot}C_6H_4{\cdot}CH{<}\overset{O}{\underset{CH\cdot CO_2Et}{|}}$, b. p. 187—191°/18 mm., and the corresponding sodium salt, which reacts with hydroxylamine hydrochloride to give the oxime of *p*-methoxyphenylacetaldehyde and carbon dioxide. Similarly, piperonaldehyde gives *ethyl 3:4-methylenedioxyphenylglycidate*, b. p. 205—210°/17 mm., and the sodium salt, which is converted into homopiperonaldoxime. These esters were expected to combine with amines to form serines, but the experiments were unsuccessful. Ethyl *carbethoxyglycine*, $CO_2Et{\cdot}NH{\cdot}CH{\cdot}CO_2Et$, was expected to combine with benzaldehyde in the presence of sodium to form the *N*-carbethoxy-derivative of the serine, but water is eliminated in the reaction, and the product is a mixture of an *acid* of a new type, $CHPh{:}C(CO_2H){\cdot}NH{\cdot}CO_2H$, silky leaflets, m. p. 187—190° (decomp.), and its *ethyl* ester, needles, m. p. 106—107° (decomp.).

The Successful Experiments.—Ethyl glycine and benzaldehyde are dissolved in ether and mixed with sodium wire. The metal is soon covered with a brown crust of the sodium salt of the phenylbenzylideneserine, $OH{\cdot}CHPh{\cdot}CH(CO_2Na){\cdot}N{:}CHPh$, which is removed frequently by means of a glass rod. After lifting out any unchanged metal, the sodium salt is dissolved in water and acidified with acetic acid, giving benzaldehyde and phenylserine, m. p. 192° (decomp.). Anisaldehyde behaves in the same way, yielding p-*anisylserine* [*a-amino-β-hydroxy-β*-p-*methoxyphenylpropionic acid*], white needles, m. p. 185—186°.

p-*Ethylcarbonatobenzaldehyde*, $CO_2Et \cdot O \cdot C_6H_4 \cdot CHO$, a pale yellow liquid, b. p. 170—172°/19 mm., m. p. 13°, from *p*-hydroxybenzaldehyde and ethyl chloroformate in the presence of sodium hydroxide, also reacts with glycine ester, but in this case very little sodium salt is produced. The main product is the ester of the arylbenzylideneserine, which remains in the ethereal solution and is hydrolysed and deposited as the *hydrochloride*, m. p. 181°, of the p-*ethylcarbonatophenylserine* ester, long, prismatic needles, m. p. 124°, on adding alcoholic hydrogen chloride. The free ester is obtained from the salt by means of ammonia solution, but the salt may be converted directly into p-*hydroxyphenylserine* [*α-amino-β*:4-*dihydroxy-β-phenylpropionic acid*], small needles or leaflets, decomp. 217°, by shaking it with *N*-sodium hydroxide.

In the case of m-*methoxy*-p-*ethylcarbonatobenzaldehyde*, m. p. 71° (from vanillin), the intermediate sodium salt is deposited in small amount, the ethereal solution only being worked up, as above. *Vanillylserine* [*α-amino-β* : 4-*dihydroxy*-3-*methoxyphenylpropionic acid*] forms slender needles, m. p. 195° (decomp.). Similarly, 3:4-*diethylcarbonatobenzaldehyde*, b. p. 215—217°/13 mm. (from protocatechualdehyde), yields the *hydrochloride* of 3:4-*diethylcarbonatophenylserine* ester,

$$C_6H_3(O \cdot CO_2Et)_2 \cdot CH(OH) \cdot CH(CO_2Et) \cdot NH_2,HCl,$$

white druses, m. p. 151—152° (decomp.), and 3:4-*dihydroxyphenylserine* [*α-amino-β*:3:4-*trihydroxyphenylpropionic acid*], m. p. 208—210° (decomp.).

Propaldehyde does not behave at all in the same way, but gives rise to a *compound* of the formula $CH_3 \cdot CH_2 \cdot CH(NH \cdot CH_2 \cdot CO_2H)_2$, which crystallises in microscopic needles, decomp. 250°.

J. C. W.

Process of Manufacturing Benzaldehyde. A. I. APPELBAUM (U.S. Pat. 1302273).—Aldehydes are produced from aromatic hydrocarbons by heating with an oxidising agent and a catalyst in the presence of an acid. For example, a mixture of 92 parts of toluene, 100 parts of manganese dioxide, 150 parts of sulphuric acid, and 5 parts of ferric, copper, or cerium sulphate is heated to boiling in a digester, then distilled with steam, and the distillate fractionated to separate benzaldehyde from unchanged toluene.

A New Method for the Conversion of Carboxylic Acids into Aldehydes. ADOLF SONN and ERNST MÜLLER (*Ber.*, 1919, **52**, [*B*], 1927—1934).—The replacement of the chlorine atom of iminochlorides by hydrogen is readily effected by the action of stannous chloride in ethereal solution; the tin double salts of the corresponding Schiff's bases appear to be formed as intermediate products, and these pass readily into aldehydes and aniline salts when heated with dilute acids, or, in certain cases, when simply treated with steam. Thus, when a solution of benzanilideiminochloride in dry ether is gradually added to pure stannous chloride dissolved in ether in the presence of dry hydrogen chloride, the *tin* salt, $C_{13}H_{12}NCl_3Sn$, lemon-yellow, crystalline powder, m. p. 165° to a

foaming mass, which becomes completely liquid at 200° (decomp.), gradually separates; it is converted by dilute hydrochloric acid into benzaldehyde, the yield being practically quantitative. Similarly, cinnamaldehyde is prepared in 92% yield from cinnamanilideiminochloride. p-*Ethylcarbonatobenzanilide*,

$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot NHPh$,

long, colourless needles, m. p. 182° (uncorr.), is transformed into the corresponding *iminochloride*, colourless, unstable needles, m. p. 1°, which yields *p*-hydroxybenzaldehyde, m. p. 115—116°. milarly, 3:4:5-*trimethoxybenzanilide*, $C_6H_2(OMe)_3\cdot CO\cdot NHPh$, lourless needles, m. p. 141°, gives successively the corresponding *inochloride*, long, unstable needles, b. p. 222—223°/13 mm., . p. 106°, and 3:4:5-trimethoxybenzaldehyde, m. p. 74—75°.

Pure stannous chloride appears to be essential for the success of the operations. Commercial grades only dissolve in ether in the presence of a large excess of hydrogen chloride, which renders the solutions unsuitable for the reduction of the more sensitive iminochlorides.

Attempts to convert aliphatic acids into aldehydes by this process have been abortive up to the present. H. W.

The *cyclo*Propane Series. VIII. Nitro*cyclo*propane Derivatives. E. P. KOHLER and H. E. WILLIAMS (*J. Amer. Chem. Soc.*, 1919, **41**, 1644—1655).—In the hope of being able to isolate some of the intermediate products which could not be examined in the earlier work (A., 1919, i, 582), the authors have turned their attention to another nitro*cyclo*propane derivative, and now describe p-*bromobenzoylphenylnitro*cyclo*propane*, which they have prepared in three of the four possible stereoisomeric forms.

p-*Bromophenyl γ-nitro-β-phenylpropyl ketone*,

$NO_2\cdot CH_2\cdot CHPh\cdot CH_2\cdot CO\cdot C_6H_4Br$,

small needles, m. p. 101—102° (*semicarbazone*, m. p. 168—169° [decomp.]), is prepared, together with the "dimolecular" *product*, $NO_2\cdot CH(CHPh\cdot CH_2\cdot CO\cdot C_6H_4Br)_2$, by the action of sodium nitromethane on α-phenyl-γ-(*p*-bromophenyl)propenone. When brominated in carbon tetrachloride solution, it yields three p-*bromophenyl α-bromo-γ-nitro-β-phenylpropyl ketones*,

$NO_2\cdot CH_2\cdot CHPh\cdot CHBr\cdot CO\cdot C_6H_4Br$,

fine needles, m. p. 114·5—115·5°, rhombic tables, m. p. 105—106°, and needles, m. p. 91°, respectively, and a *dibromo-compound*, thin flakes, m. p. 138—139°. Bromination in the α-position to the nitro-group is effected by means of the sodium derivative, whereby p-*bromophenyl γ-bromo-γ-nitro-β-phenylpropyl ketone*,

$NO_2\cdot CHBr\cdot CHPh\cdot CH_2\cdot CO\cdot C_6H_4Br$,

is obtained in needles, m. p. 127°, whilst the corresponding γγ-dibromo-*product* forms thin plates or needles, m. p. about 144—146°. Since it has been previously shown that it is possible to distinguish between bromine compounds in which the bromine is in the α-position to the nitro-group and those in which it is in the α-position relative to the carbonyl by treatment with potassium

iodide, the former undergoing reduction, whilst the latter ar transformed into the corresponding iodo-derivatives, the foregoin bromo-derivatives have been boiled with potassium iodide i alcoholic solution; the reaction is found to be a general one, an the following substances are obtained: p-*bromophenyl α-iodo-γ nitro-β-phenylpropyl ketone*, pale yellow, rhombic plates, m. p 110°, from the isomerides, m. p. 114·5—115·5° and 105—106° respectively; the nitro-ketone from the γ-monobromo-derivative and first the γ-monobromo-compound, m. p. 127°, and then th nitro-ketone from the γγ-dibromo-derivative.

3-Nitro-2-p-bromobenzoyl-1-phenylcyclopropane,

$$CHPh\langle{}^{CH\cdot CO\cdot C_6H_4Br}_{CH\cdot NO_2},$$

m. p. 131°, is obtained by the action of fused potassium acetate on an alcoholic solution of the α-bromo-compound; similar treatment of the γ-bromo-compound leads to the formation of an isomeric *cyclo*propane derivative, fine needles, m. p. 115°, possibly formed as a result of prolonged contact with potassium acetate, since the same substance is formed from the isomeride, m. p. 130°, under similar conditions. A third *isomeride*, needles, m. p. 162—163°, is formed when an alcoholic suspension of either of the other two is treated with very dilute sodium methoxide solution. All three substances give the corresponding open-chain, saturated nitro-ketone, colourless needles, m. p. 101°, when reduced with zinc dust and alcohol. The substance, m. p. 130°, readily combines with hydrochloric acid, giving *p-bromophenyl γ-chloro-β-nitro-γ-phenylpropyl ketone*, $CHPhCl\cdot CH(NO_2)\cdot CH_2\cdot CO\cdot C_6H_4Br$, long, slender needles, m. p. 133°, which on treatment with potassium acetate loses nitrous acid, yielding a mixture of stereoisomeric p-*bromophenyl γ-chloro-γ-phenylallyl ketones*, downy needles, m. p. 179—180°, and yellow plates, m. p. 108—109°, the constitution of which is deduced from the fact that either is converted by permanganate into benzoic and *p*-bromobenzoic acids, and by ozone into *p*-bromobenzoic acid and benzoyl chloride. The hydrochloric acid additive product readily loses hydrogen chloride and nitrous acid when boiled in alcoholic solution, and yields *2-phenyl-5-p-bromophenylfuran*,

$$O\langle{}^{CPh=\!=\!=CH}_{C(C_6H_4Br):CH},$$

colourless or very pale yellow flakes, m. p. 127°. The *cyclo*propane derivatives, m. p.'s 130° and 162° respectively, readily unite with hydrogen bromide, and, according to the manner in which the experiment is conducted, yield two *substances*, $C_{16}H_{13}O_3NBr_2$, colourless needles, m. p. 144° (decomp.), and long needles, m. p. 133°, which are similarly constituted to the hydrogen chloride additive compound, since, like this, they readily pass into the same 2-phenyl-5-*p*-bromophenylfuran. On the other hand, they lose halogen acid more easily than nitrous acid when treated with potassium acetate,

yielding p-*bromophenyl β-nitro-γ-phenylallyl ketone*,

$CHPh:C(NO_2)·CH_2·CO·C_6H_4Br$,

unstable colourless needles, m. p. 162—163° (decomp.).

The *cyclo*propane derivatives react slowly with bromine when dissolved in boiling carbon tetrachloride and placed in direct sunlight. In this manner, the isomeride, m. p. 130°, yields two isomeric p-*bromophenyl αγ-dibromo-β-phenylpropyl ketones*,

$C_{16}H_{12}O_3NBr_3$,

m. p.'s 162—163° and 137° respectively, which can also be prepared by the action of bromine on the γ-bromo-additive product of hydrogen bromide and the *cyclo*propane derivative. (A third *substance*, $C_{16}H_{12}OBr_4$, fine crystalline powder, m. p. 190—193°, which is probably a furan derivative, is also obtained.) When treated with potassium iodide, the bromine additive compounds yield p-*bromophenyl β-nitro-γ-phenylpropenyl ketone*, yellow plates, m. p. 115°, the constitution of which follows from its oxidation to *p*-bromobenzoic and phenylacetic acids.

The action of dilute sodium methoxide solution in converting the *cyclo*propane derivatives of lower m. p. into the isomeride of highest m. p. is somewhat difficult to interpret, but by cautious regulation of the reaction it has been found possible to isolate the methoxy-*compound*, $CH_2Ph·C(OMe):CH·CO·C_6H_4Br$, thin needles, m. p. 102—103°, which is a possible intermediate product; the composition of the substance is deduced from its oxidation by permanganate in acetone solution to methyl phenylacetate and *p*-bromobenzoic acid. It is easily hydrolysed by hydrochloric acid to p-*bromobenzoylphenylacetylmethane*,

$CH_2Ph·CO·CH_2·CO·C_6H_4Br$,

rhombic plates, m. p. 80—81°, which readily gives a pale green *copper* derivative. H. W.

The *cyclo*Propane Series. IX. Nitro*cyclo*propane Derivatives. ELMER PETER KOHLER and M. SRINIVASA RAO (*J. Amer. Chem. Soc.*, 1919, **41**, 1697—1704).—The nitro*cyclo*propane derivatives described previously have all contained an aryl group; the authors now describe a similar compound with an alkyl group, and, in order to avoid complications in the preparation, have used *tert*.-valeryl compounds, the substance studied being 3-nitro-2-*tert*.-butyryl-1-phenyl*cyclo*propane, $CHPh<\begin{matrix}CH·NO_2\\ |\\ CH·CO·CMe_3\end{matrix}$ which is prepared by the usual methods. The substitution of the *tert*.-butyl- for the phenyl-group does not materially affect the properties of the *cyclo*propane derivative, and, unfortunately, does not lower the boiling points of the substances sufficiently to make distillation under reduced pressure feasible. The new *cyclo*propane readily combines with other substances, and the ring opens in all cases between the carbon atoms attached to the phenyl and trimethylacetyl groups.

γ-*Nitro-β-phenylpropyl* tert.-*butyl ketone*,

$NO_2·CH_2·CHPh·CH_2·CO·CMe_3$,

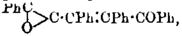
minute, colourless plates, m. p. 74°, is prepared by the action of sodium

methoxide on benzylidenepinacoline and nitromethane. When brominated in carbon tetrachloride solution it yields two isomeric *α-bromo-γ-nitro-β-phenylpropyl* tert.*-butyl ketones*, large needles, m. p. 143—144°, and colourless plates, m. p. 74—75°, the latter of which is readily transformed into the former by boiling with methyl-alcoholic potassium acetate. Both isomerides are slowly converted into *3-nitro-2-*tert.*-valeryl-1-phenyl*cyclo*propane*, cubes, m. p. 94°, by the regulated action of potassium acetate in boiling methyl alcoholic solution. This substance readily loses nitrous acid under the influence of alkalis, and yields *phenylacetyl-*tert.*-valerylmethane*, $CH_2Ph\cdot CO\cdot CH_2\cdot CO\cdot CMe_3$, needles, m. p. 44°, which has also been directly synthesised from ethyl phenylacetate and pinacoline. With phenylcarbimide it yields a *phenylcarbamate*, m. p. 130—132°, and with hydroxylamine it gives *5-benzyl-3-*tert.*-butyl*iso*oxazole*, m. p. 51°, and *3-benzyl-5-*tert.*-butyl*iso*oxazole*, m. p. 63°. The nitro*cyclo*propane combines very readily with hydrogen bromide to form *γ-bromo-β-nitro-γ-phenylpropyl* tert.*-butyl ketone*, $CHPhBr\cdot CH(NO_2)\cdot CH_2\cdot CO\cdot CMe_3$, very unstable crystals, m. p. 66—67°, which readily lose both nitrous acid and hydrogen bromide; with cold potassium acetate, however, chiefly the latter is eliminated with production of *β-nitro-β-benzylidene-ethyl* tert.*-butyl ketone*, $CHPh:C(NO_2)\cdot CH_2\cdot CO\cdot CMe_3$, long, yellow unstable needles, m. p. 53—54°, in which the double bond must be adjacent to the phenyl group, since benzaldehyde is formed as primary product of its oxidation by permanganate in acetone solution. When the unsaturated nitro-ketone is treated with hydrogen bromide in glacial acetic acid solution, it not only unites with the acid, but also undergoes reduction, yielding *5-bromobenzyl-3-*tert.*-butyl*iso*oxazole*, needles, m. p. 77—78°, which is reduced by zinc dust and acetic acid to 5-benzyl-3-*tert*.-butyl*iso*oxazole, m. p. 50°.

H. W.

Pyrylium Compounds. V. Enolic and Ketonic Forms of Unsaturated 1 : 5-Diketones. W. Dilthey and Th. Böttler (*Ber.*, 1919, **52**, [*B*], 2040—2054).—The conversion of the condensation product of phenyl styryl ketone and deoxybenzoin into a pyrylium salt has been previously described (A., 1917, i, 578). The *pseudo*-base corresponding with the latter has now been investigated and is shown to be α-hydroxy-ε-keto-αγδε-tetraphenyl-$\Delta^{\alpha\gamma}$-pentadiene, $OH\cdot CPh:CH\cdot CPh:CPh\cdot COPh$; when treated with a moderate amount of alkali, it readily passes into the corresponding diketones. The first case of keto-enolic desmotropy in unsaturated 1:5-diketones is thus presented.

2:3:4:6-*Tetraphenylpyryl ferrichloride*, $C_{29}H_{21}OCl_4Fe$, yellow, shining prisms, m. p. 186°, is prepared by adding hydrated ferric chloride to a warm solution of αε-diketo-αγδε-tetraphenylpentane in acetic acid and acetic anhydride. When warmed with water in the presence of ether, it gives *α-hydroxy-ε-keto-αγδε-tetraphenyl-$\Delta^{\alpha\gamma}$-pentadiene*, pale yellow needles, united in clusters, m. p. 112—113°, from which the iron salt is readily re-formed. It does

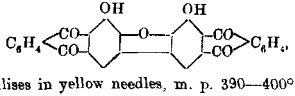
not dissolve in aqueous alkalis, but forms deep violet solutions with alcoholic alkalis. It is rapidly transformed by alcoholic ammonia into 2:3:4:6-tetraphenylpyridine, m. p. 182°. It is rapidly oxidised by permanganate in pyridine solution, yielding benzoic acid, benzoylformic acid, and benzil. Acetylation with acetic anhydride and sodium acetate leads to the formation of *αε-diketo-β-acetyl-αγδε-tetraphenyl-Δ^γ-pentene*, COPh·CHAc·CPh:CPh·COPh, needles, m. p. 172—173°, which gives the ketone, m. p. 142° (*v.c.*), when hydrolysed with alcoholic potassium hydroxide. Attempts to obtain benzoyl- or alkyl-derivatives were unsuccessful. Semicarbazide yields a *mono-semicarbazone*, short, colourless prisms, m. p. 225—226° (decomp.). The enol reacts but slowly with bromine at the ordinary temperature, but, at 30°, the latter is decolourised, and a *substance*, pale yellowish-green prisms, m. p. 166—167°, is formed to which the constitution  is ascribed. The following salts of the *pseudo*-base are described: *platinichloride*, $C_{58}H_{42}O_2Cl_4Pt$, orange-yellow leaflets, m. p. 229—230°; *zincochloride*, lemon-yellow leaflets, m. p. 295—296°; *stannichloride*, yellow needles, m. p. 134—135°; *perchlorate*, canary-yellow, shining needles, m. p. 261°; *periodide*, $C_{29}H_{21}OI_3$, brownish needles, m. p. 218°; *perbromide*, short, yellow needles, m. p. 217° (also obtained but with greater difficulty from the isomeride, m. p. 142°); *hydrogen bromide*, yellow prisms which when rapidly heated eliminate hydrogen bromide at about 150° and finally melt at 233—235°; *normal bromide*, coarse, orange-red prisms, m. p. 237—238°.

The enolic form is quantitatively converted into *αε-diketo-αγδε-tetraphenyl-Δ^γ-pentene*, COPh·CH_2·CPh:CPh·COPh, when its solution of methyl alcohol is gently warmed with a solution of sodium (1 atom) in the same solvent; it forms colourless, shining needles, m. p. 142—143°, and is less soluble than the enol in all solvents. It is much more stable than the enolic form both towards permanganate and towards bromine; with the latter, however, it slowly yields the same substance, m. p. 166°, which is obtained from the enol. It slowly yields the pyrylium salts which are instantly formed from the enolic variety. Acetylation converts it into the same acetyl derivative as is obtained from the enol. Semicarbazide slowly yields the α-semicarbazone of αε-diketo-αγδε-tetraphenyl-Δ^γ-pentene (see above). [A similar slow reaction is observed with the corresponding saturated diketone, whereby the *α-semicarbazone* of *αε-diketo-αγδε-tetraphenylpentane*, m. p. 238—239°, is produced.] The ketonic is converted into the enolic form by the action of an excess of alcoholic potassium hydroxide. H. W.

Preparation of Benzoquinone. JOHN M. WEISS and CHARLES R. DOWNS (U.S. Pat. 1318631).—Benzoquinone is produced by subjecting benzene in the vapour phase to the action of a gas containing oxygen at a suitable temperature and in the presence of a catalyst. G. F. M.

Reduction of Dihydroxythymoquinone by means of Palladium Hydrogen. NELLIE A. WAKEMAN (*J. Amer. Chem. Soc.*, 1919, **41**, 1873—1875). Thymoquinone is very readily reduced by hydrogen in alcoholic solution in the presence of palladium chloride with the formation of hydrothymoquinone. Similar attempts to reduce dihydroxythymoquinone in alcoholic or ethereal solution were only partly successful, since, although reduction occurred very readily and the solutions became decolorised, the product reverted so easily to the red dihydroxythymoquinone that its isolation in the pure condition was impossible. By performing the experiment in acetic anhydride solution, however, it was found that reduction occurs with less rapidity, but gives an almost quantitative yield of the desired *tetra-acetyl* derivative, colourless, prismatic crystals, m. p. 180—182°, which is stable in air and, on hydrolysis, yields dihydroxythymoquinone in practically quantitative amount. The palladium chloride appears to suffer no loss of activating power when used repeatedly in these experiments. H. W.

Action of Potassium Hypochlorite on Alizarin in Alkaline Solution. R. SCHOLL [with EMIL SCHWINGER and ALB. KABATSCHNIK] (*Ber.*, 1919, **52**, [*B*], 1829—1836. Compare A., 1919, i, 25, 406).—Whereas alkaline ferricyanide solutions cause rupture of the hydroxylated ring of alizarin, the oxidative activity of hypochlorites is manifested in the production of dianthraquinonyl derivatives. The oxidation may be performed by adding potassium hypochlorite solution to a solution of alizarin in potassium hydroxide, or by dissolving the substance in 8% potassium hydroxide and passing in chlorine. The chief product separates as a bluish-black *potassium* salt which is decomposed by dilute sulphuric acid and the acid purified by boiling with nitrobenzene. The product, 3 : 4 : 3′ : 4′-*tetrahydroxy*-2 : 2′-*dianthraquinonyl*, $C_{28}H_{14}O_8$, forms dark yellowish-red, microscopic, rhombic or hexagonal, prismatic tablets, m. p. 384—395°, and its *sodium* salt is dark blue. It has no affinity for un-mordanted fibres, and is much poorer as a mordant dye than alizarin. The *tetra-acetate* forms yellow crystals, m. p. 278—280°. When distilled with zinc dust in an atmosphere of hydrogen, under 15—30 mm. pressure, it yields 2 : 2′-*dianthryl*, $C_{28}H_{18}$, yellow, rhombic leaflets, with green fluorescence, m. p. 355°, which is also formed when 2 : 2′-dianthraquinonyl (A., 1911, i, 453) is treated in the same way. 1 : 1′-Dianthraquinonyl, however, does not yield the unknown 1 : 1′-dianthryl under these conditions, but rather *meso*-naphthadianthrone (A., 1910, i, 494). When heated with zinc chloride, the tetrahydroxydianthraquinonyl gives 4 : 4′-*dihydroxy*-2 : 2′-*dianthraquinonylene*-3 : 3′-*oxide*,



which crystallises in yellow needles, m. p. 390—400° (decomp.). J. C. W.

Synthesis of some Homologues of the Terpenes: Derivatives of 1 : 4-Di*iso*propyl*cyclo*hexane. MARSTON TAYLOR BOGERT and CLARENCE PEAVY HARRIS (*J. Amer. Chem. Soc.*, 1919, **41**, 1676—1690).—The peculiar properties of the terpenes appear to be generally associated with the presence of an *iso*propyl and a methyl group, and seem to be due to the former rather than the latter; whilst numerous derivatives having one such group have been investigated, little is known of the effect of two of these groups. The authors have therefore investigated a series of homologues of *p*-di*iso*propylbenzene, which are prepared by the action of magnesium methyl iodide on the methyl ester of terephthalic and partially hydrogenated terephthalic acids and subsequent elimination of water if necessary.

p-*Dihydroxy*iso*propylbenzene*, $C_6H_4(CMe_2\cdot OH)_2$, colourless, short, lustreless needles, m. p. 142·4—142·9° (corr.), is obtained from magnesium methyl iodide and methyl terephthalate (the method of achieving the regulated addition of the reagent to the ester, which is only sparingly soluble in ether, is fully described in the original); when distilled with potassium hydrogen sulphate under diminished pressure, it yields 1 : 4-*di*iso*propenylbenzene*, micaceous plates, m. p. 63·6—64° (corr.), which readily unites with four atoms of bromine without evolution of hydrogen bromide (the *tetrabromide* could not be isolated in the pure condition). Similarly, methyl $\Delta^{1,4}$-dihydroterephthalate, m. p. 128·4—129·4° (corr.), yields 1 : 4-*di*iso*propenyl*-$\Delta^{1,4}$-cyclo*hexadiene*, plates, m. p. 117—117·5° (corr.), the dicarbinol formed as an intermediate product eliminating water spontaneously. The substance adds four atoms of bromine, but hydrogen bromide is readily evolved; however, by suitable adjustment of conditions, a small quantity of the *tetrabromide*, cubic crystals, m. p. 107—109° (corr.), was isolated.

The main product of the action of the Grignard reagent on methyl Δ^1-tetrahydroterephthalate, b. p. 153·3—154·5° (corr.)/20 mm., m. p. 35·2—36·2° (corr.), appears to be the corresponding dicarbinol which, however, could not be isolated in the pure condition. The crude product was therefore dehydrated with potassium hydrogen sulphate, whereby two isomeric *hydrocarbons*, $C_{12}H_{18}$, b. p.'s 95—98°/20 mm. and 105—108°/20 mm. respectively, were produced. Both are colourless oils, which become viscous and slightly yellow on prolonged exposure to air. Both absorb bromine quickly at the outset, but evolution of hydrogen bromide soon begins, so that no pure bromine derivatives could be separated.

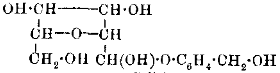
The densities, refractive indices, and magnetic rotatory powers of the new hydrocarbons in the pure state and in a number of solvents have been determined, and the data are discussed with reference to their bearing on the structures assigned to these compounds.

H. W.

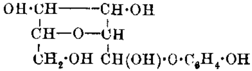
Constituents of Resins. Degradation of *d*-Sumaresinolic Acid. ALOIS ZINKE (*Monatsh.*, 1919, **40**, 277—280).—When *d*-sumaresinolic acid is oxidised by chromic acid in glacial acetic acid solution, a monocarboxylic *acid*, $C_{27}H_{40}O_4$, is obtained, which is

isomeric with the acid obtained from *d*-siaresinolic acid (A., 1919, i, 129); it is best purified by crystallisation from benzene, from which it separates in coarse prisms $+C_6H_6$, the solvent being only completely expelled at 150° in a vacuum. The pure substance has m. p. 260—261°. The *barium* salt is described. When thus oxidised, *d*-sumaresinolic acid loses three carbon and eight hydrogen atoms; hence it probably contains a propyl or *iso*propyl group, and its formula may be written $C_{26}H_{40}O_2(C_3H_7)\cdot CO_2H$. H. W.

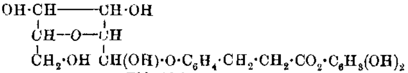
The Distillation of certain Glucosides under Reduced Pressure. AMÉ PICTET and HENRY GOUDET (*Helv. Chim. Acta*, 1919, **2**, 698—703).—The fact that the majority of the naturally occurring glucosides are lævorotatory, although yielding dextrose on hydrolysis, has led the authors to doubt whether they are in reality derivatives of the latter substance. To throw light on the question, they have distilled salicin, arbutin, and phloridzin under reduced pressure, and, in each case, have isolated lævoglucosan (compare Tanret, A., 1894, i, 564; Pictet and Sarasin, A., 1918, i, 59) from among the products of distillation. They are therefore led to suggest the annexed formulæ for the glucosides:



Salicin.

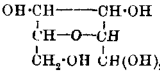


Arbutin.



Phloridzin.

Hydrolysis of the glucosides by barium hydroxide solution yields primarily an unstable hydrate (annexed formula), which passes into lævoglucosan by loss of water. With acids, the rupture of the ring also occurs with formation of dextrose.



Salicin, on distillation, yielded an aqueous liquid containing a little furfuraldehyde, and a pasty mass from which lævoglucosan, m. p. 179—180°, $[\alpha]_D^{20}$ −66·73° in aqueous solution, was isolated. Arbutin gave an aqueous liquid containing acetic acid and furfuraldehyde, and a pasty mass from which lævoglucosan and quinol were obtained, whilst phloretic acid, phloroglucinol, and lævoglucosan were isolated from the semi-solid product from phloridzin. **H. W.**

Chemistry and Pharmacology of Aloes. I. Products of the Oxidation of the Constituents of Aloes by means of Alkali Persulphate. EUGEN SEEL (*Arch. Pharm.*, 1919, **257**, 212—228. Compare A., 1901, i, 92; 1917, i, 41, 577).—The constituents of aloes of pharmacological importance are: (1) Aloin, which is crystalline and soluble in water; (2) aloëtin, which is amorphous and soluble in water; (3) resin or crude resin, which is amorphous and insoluble in water in the cold; (4) emodin, which occurs to the extent of less than 1%, and is very sparingly soluble even in hot water. The products obtained when the first three of these components are oxidised with potassium or ammonium persulphate have been studied.

In the case of aloin, the oxidation proceeds most simply and smoothly in very dilute aqueous solution, a series of colour changes taking place. According as the reaction is slow or rapid, it yields puraloin I either alone or mixed with puraloin II. These two products form red or brownish-red, amorphous powders, and have not been obtained quite free from ash. The results of analyses and molecular weight determinations of their derivatives indicate the formulæ, $C_{12}H_{10}O_6$ for puraloin I, and $C_{13}H_{12}O_6$ for puraloin II. Both are partly hydrated, and they dissolve in alkalis or concentrated acids, giving faintly violet-red or reddish-brown colorations; they are not resolved by acids, but are converted to a greater or less extent into a black powder, termed puralonigrin, owing to its analogy to alonigrin. The formulæ indicate the absence from the puraloins of an anthraquinone nucleus, and puraloin I is regarded as a dihydroxymethyldihydronaphthaquinonecarboxylic acid, and puraloin II as a dihydroxymethyldihydronaphthaquinoneacetic acid. Quantitative study of the oxidation of aloin by persulphate indicates that the sugar-residue of the glucoside is oxidised to carbon dioxide, and that part of the anthraquinone ring also undergoes attack. Since the oxidation products are insoluble in water and dilute acid, and are thus precipitated and protected from further oxidation, the reaction lends itself to the quantitative evaluation of aloes.

Oxidation of aloin by persulphate in alkaline solution yields products which are more untractable than the puraloins, and have not been investigated in detail.

Puraloin I, which is insoluble in 96% alcohol, blackens at 230—240°, and sinters and decomposes at about 340—350°. *Puraloin II* differs from puraloin I principally in its solubility in 96% alcohol. Both are capable of acetylation, the products being non-crystalline and possessed of a marked tendency to form colloidal solutions. *Triacetylpuraloin I*, $C_{12}H_7O_6Ac_3$, is yellowish-brown, and sinters and turns brown at 180—190°. *Diacetylpuraloin II* (?), $C_{13}H_{10}O_6Ac_2$, is brown, and remains unchanged at 300°. On benzoylation, puraloin I yields a reddish-yellow powder which is intermediate in composition between the di- and tribenzoyl derivatives, and gradually decomposes and blackens at above 200°. *Dibenzoylpuraloin II*, $C_{13}H_{10}O_6Bz_2$, forms a reddish-yellow

powder, and sinters at 220° and carbonises at a higher temperature. Both puraloins yield ochre-yellow *monobromo*-derivatives, $C_{12}H_9O_6Br$ and $C_{13}H_{11}O_6Br$ respectively, which gradually darken at above 200°.

The action of persulphate on aloëtin yields principally puraloins I and II, but the proportions of secondary products are greater than those obtained from aloin. Oxidation of the crude resin also yields the two puraloins.

When administered in single doses of 0·5—2·0 grams, the puraloins exert a mild laxative action, which occasionally fails, but is most trustworthy with children and dogs. T. H. P.

Chemistry and Pharmacology of Aloes. II. Products of the Oxidation of the Constituents of Aloes by Caro's Acid. EUGEN SEEL (*Arch. Pharm.*, 1919, **257**, 229—254. Compare A., 1901, i, 92; 1917, i, 577, and preceding abstract).—Of the products obtained by oxidising aloin by means of Caro's acid, the following have been identified: (1) A small proportion of trihydroxymethylanthraquinone, m. p. 223—224°, already known. (2) Two isomeric tetrahydroxymethylanthraquinones, m. p. 185—190° and 232—234° respectively, not previously described in the literature. (3) Numerous hydrogenated tri- and tetra-hydroxymethylanthraquinones, which form products intermediate to aloin and the anthraquinone derivatives, but are not obtained in sufficient quantities to admit of isolation. (4) Three naphthalene derivatives, the compositions of which have not been determined. (5) A compound which was isolated in the form of its bromo-derivative, and may be a derivative of either anthracene or naphthalene.

Tetrahydroxymethylanthraquinone, $C_{15}H_{10}O_5$, forms red crystals, m. p. 185—190°, and its *isomeride*, red crystals, m. p. 232—234°. Acetylation of these compounds yields mostly tarry masses, from which only a small proportion of *tetra-acetyl* derivative, $C_{15}H_6O_6Ac_4$, is obtainable as a bright yellow, crystalline powder, m. p. 196—198°; this acetyl derivative dissolves in concentrated sulphuric acid to a violet solution, and on hydrolysis yields the tetrahydroxymethylanthraquinone, m. p. 232—234°. Benzoylation of the two compounds gives (1) a tetrabenzoyl derivative, $C_{15}H_6O_6Bz_4$, which forms a pale ochre-yellow, microcrystalline powder, m. p. 236—238°, dissolves in concentrated sulphuric acid to a violet-red solution, and on hydrolysis yields the tetrahydroxymethylanthraquinone, m. p. 232—234°; (2) a *compound*, m. p. 225—226°, which differs appreciably in composition from the tetrabenzoyl derivative, and on hydrolysis gives only the tetrahydroxymethylanthraquinone, m. p. 232—234°, although it is obtained from the isomeride with m. p. 185—190°. Whether the latter is isomeric with the compound, m. p. 232—234°, or merely an impure form of it, is still uncertain.

After complete extraction of the oxidation products of aloin with chloroform or ether, extraction with 90—96% alcohol removes a compound which blackens slowly at above 240° and agrees approximately in composition with puraloin I, although in solu-

bility in strong alcohol it corresponds with puraloin II. This compound yields an *acetyl* derivative, $C_{12}H_5O_6Ac_3$ or $C_{12}H_7O_6Ac_3$, which forms yellowish-white flocks, m. p. 115—120°, and a *tribenzoyl* derivative, $C_{12}H_5O_6Bz_3$ or $C_{12}H_7O_6Bz_3$, which sinters at 220° and melts and decomposes at 240°. A compound of similar composition to that soluble in strong alcohol may afterwards be extracted from the oxidation products by means of dilute alcohol.

The action of Caro's acid on aloëtin yields: (1) Trihydroxymethylanthraquinone, m. p. 223—224°. (2) A tetrahydroxymethylanthraquinone agreeing in properties with the compound, m. p. 232—234°, but having m. p. 215°. (3) A compound, $C_{13}H_{10}O_6$, which has no sharp melting point, and yields a diacetyl derivative, apparently with simultaneous loss of water, and a dibenzoyl derivative, $C_{13}H_8O_6Bz_2$, showing incipient fusion at 225° and carbonisation at a higher temperature. (4) A small proportion of a dark brown powder which does not melt sharply, but blackens at a high temperature, and has approximately the composition of puraloin I. (5) A compound separable as its bromo-derivative, which darkens at 180°, but does not melt at 290°, and has the properties, but not the composition, of the bromo-derivative similarly obtained from the oxidation products of aloin.

The products obtained when the resin is oxidised by means of Caro's acid indicate that this resin consists mostly of resinified aloëtin, together with a little resinified aloin.

Oxidation of emodin by Caro's acid yielded no well-defined products, but the results obtained show that emodin is not readily converted into a tetrahydroxymethylanthraquinone in this way.

Trihydroxymethylanthraquinone or emodin acts as a mild purgative, without secondary effects, when administered to man and animals in doses of 0·2—0·4 gram at intervals of three hours, whereas smaller doses often produce such secondary effects and are sometimes without purgative action. Tetrahydroxymethylanthraquinone or hydroxyemodin has a weaker purgative effect than emodin, doses of 0·5 gram being often necessary; like emodin, it may be administered subcutaneously. T. H. P.

Chemistry and Pharmacology of Aloes. III. Products of the Oxidation of the Constituents of Aloes by Hydrated Sodium Peroxide. EUGEN SEEL (*Arch. Pharm.*, 1919, **257**, 254—259).—Oxidation of aloin by means of sodium peroxide yields emodin and a residue which, when treated with bromine, gives a crystalline *dibromo*-derivative, darkening at about 145°, m. p. 160—162° (decomp.), corresponding in composition with a dibromide of puraloin I, $C_{12}H_8O_6Br_2$. Thus, by sodium peroxide in alkaline solution, aloin is only partly resolved into emodin, the greater part of the molecule, including the sugar residue, being attacked only by persulphate. These results confirm the glucosidic character of aloin (compare Léger, A., 1904, i, 907).

The action of sodium peroxide on aloëtin is similar to that on aloin, the yield of emodin being very small; with the crude resin,

also, only small proportions of emodin are obtained. Emodin itself is not oxidised further by sodium peroxide, but may be partly purified, only the anthraquinone derivative remaining unaltered.

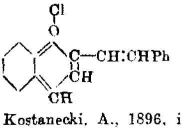
T. H. P.

Anemonin. III. Constitution of Anemolic Acid. Y. ASAHINA and A. FUJITA (*Yakugaku Zasshi* [*J. Pharm. Soc. Japan*], 1919, **448**, 471—484).—Anemonin suspended in methyl alcohol and reduced with 3% sodium amalgam and glacial acetic acid at 5° gave *dihydroanemonin*, $C_{10}H_{10}O_4$, m. p. 172°, in 80—90% yield, which exhibits a normal molecular weight in freezing phenol. It is easily transformed by heating with hydrochloric acid into *anemolic acid*, $C_{10}H_{14}O_6$, which yields a *disemicarbazone*, $C_{12}H_{20}O_8N_8$, m. p. 158°. When the acid is dissolved in ammonia, it gives a precipitate, $C_{10}H_{16}O_4N_2$, which has m. p. 195° after recrystallisation from hot water, gives the pine-shaving reaction, and with hydrochloric acid yields pyrrole-2:5-dipropionic acid, m. p. 170°. From these facts, the authors conclude that anemolic acid is identical with dilævulinic acid, a conclusion confirmed by comparison with the substances synthesised by Kehrer and Hofacker's method (A., 1897, i, 214). On the other hand, sebacic acid, m. p. 131°, is obtained when dihydroanemonin is reduced with platinum black and hydrogen. So far as is known, dihydroanemonin ought to have a constitution similar to that of angelicolactone. Dihydroanemonin when boiled with anisaldehyde and aniline yields a light yellow condensation product, $C_{26}H_{22}O_6$, m. p. 200°. CHEMICAL ABSTRACTS.

The Tinctorial Properties of some Anthocyanins and certain Related Compounds. I. ARTHUR E. EVEREST and ARCHIBALD J. HALL (*J. Soc. Dyers*, 1919, **35**, 275—279).—The authors record dyeing tests of various anthocyanins and anthocyanidins, and of the colouring matters of the viola, rose, lupin, pelargonium, sweet pea, bilberry, black currant, cranberry, and radish.

An improved process is given for the preparation of 2-*o*-hydroxystyrylbenzopyrylium chloride, which the authors find to have the formula $C_{17}H_{13}O_2Cl,2H_2O$ (compare Decker and Felser, A., 1908, i, 906, who give $1H_2O$).

When salicylaldehyde is condensed with styryl methyl ketone, yellow crystals of a *substance*, possibly of the annexed formula, are obtained, but could not be satisfactorily analysed. Contrary to the statement of Harries and Busse (A., 1896, i, 301), *o*-hydroxybenzylidenediacetophenone (Bablich and Kostanecki, A., 1896, i, 239; Cornelson and Kostanecki, A., 1896, i, 240) is produced by condensing acetophenone and salicylaldehyde by means of 10% sodium carbonate solution.



J. C. C.

Experimental Studies on Plant Pigments. B. HARROW and W. J. GIES (*Proc. Soc. Expt. Biol. Med.*, 1918, **16**, 8—10).—Observations are reported on (*a*) flavones, a group of yellow pig-

ments characterised by the production, in their solutions, of intense yellowish-brown colour on the addition of aqueous ammonia, and of (*b*) anthocyanins, a group of red, violet, or blue pigments, which in solution change to bluish-green on the addition of acid. These pigments were obtained from tulips. Active (nascent) hydrogen reduces flavone to anthocyanin. The latter can be further reduced to a leuco-base, which in turn, by exposure to air, or more rapidly by addition of an oxidising agent, is reconverted into anthocyanin. Anthocyanin, isolated in a fairly pure condition by Willstätter's method, has been oxidised to flavone with the aid of hydrogen peroxide. Flavone thus obtained from anthocyanin can be reduced again to anthocyanin. Anthocyanin when extracted with alcohol made anhydrous with copper sulphate yields a red extract, whereas if the extraction is made with alcohol rendered anhydrous with calcium oxide, a green solution is obtained. Anthocyanin, prepared according to Willstätter's method and dissolved in absolute alcohol, was compared with phenolphthalein, and found to be its equal in point of delicacy. It is superior in that a change from alkali to acid is indicated by a sharp change from green to red, and not from red to no colour at all. CHEMICAL ABSTRACTS.

Furyl Alkyl Ketones. K. MONOYA (*J. Pharm. Soc., Japan*, 1919, **447**, 357—401).—The relation between the constitution of furyl alkyl ketones and their optical properties, and also their action with sodium and alkyl nitrite, have been investigated. The ketones were prepared from furancarboxylonitrile (pyromuconitrile) and magnesium alkyl haloids in dry ether, the intermediate products being decomposed by heating with sulphuric acid and a little oxalic acid. Thus were prepared *furyl benzyl ketone*, plates, m. p. 47—48° (*oxime*, m. p. 125—126°; *semicarbazone*, m. p. 171—172°), furyl methyl ketone, $D_4^{20·3}$ 1·0977, n_D 1·50177, furyl ethyl ketone, $D_4^{20·5}$ 1·0587, n_D 1·49623, furyl propyl ketone, $D_4^{11·4}$ 1·0416, n_D 1·49970, furyl *iso*butyl ketone, $D_4^{14·8}$ 1·0160, n_D 1·49488, and furyl *iso*amyl ketone, D_4^{11} 0·9988, n_D 1·49260. The exaltation of the molecular refraction of the ketones increases with the molecular weight. During the preparation of the last two ketones, *ketimines* were isolated in the form of double *compounds* with ammonium chloride, $2C_4H_3O·C(:NH)·C_4H_9,NH_4Cl$, m. p. 285—291°, and $2C_4H_3O·C(:NH)·C_5H_{11},NH_4Cl$, m. p. 268—270°. Since these are easily converted into the ketones by treatment with hydrochloric acid, the formation of the latter is represented by the scheme:

$$C_4H_3O·CN + MgRX \longrightarrow C_4H_3O·CR:N·MgX \longrightarrow C_4H_3O·CR:NH \longrightarrow C_4H_3O·COR.$$

Ethyl pyromucate, pyromucic acid, β-benzaldoxime, and oximinodeoxybenzofuroin are formed when furyl benzyl ketone is treated with ethyl nitrite and sodium in dry ether at −13°; the products are isolated by neutralising the mixture with 1% sodium hydroxide, extracting with ether, saturating the aqueous solution with carbon

dioxide, and then acidifying it with hydrochloric acid. The course of the decomposition is represented thus:

$C_4H_3O{\cdot}CO{\cdot}CH_2Ph + OEt{\cdot}NO = C_4H_3O{\cdot}CO{\cdot}CHPh{\cdot}NO + EtOH$

(EtOH)

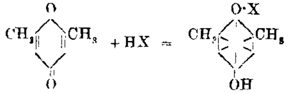
$C_4H_3O{\cdot}CO{\cdot}CPh{:}N{\cdot}OH \quad C_4H_3O{\cdot}CO_2Et + CH_2Ph{\cdot}NO[\longrightarrow CHPh{:}N{\cdot}OH]$

Furyl amyl ketone yields valeraldoxime, and the other ketones yield similar products when treated in this manner. By treatment with sodium and amyl nitrite, menthone yields γ-keto-βζ-dimethyloctoic acid (semicarbazone, m. p. 151—152°).

CHEMICAL ABSTRACTS.

Optical Chemical Notes on the Oxonium Salts of Pyrones and Thiopyrones. A. HANTZSCH (*Ber.*, 1919, **52**, [*B*], 1535—1544).—The absorption curves of a number of pyroxonium salts are discussed.

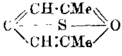
2:6-Dimethyl-1:4-pyrone shows the rudiments of an absorption band at about 1/λ=3600 in concentrated alcoholic solutions, that is, in the region of the acetone band. This ketone band disappears when the pyrone is dissolved in concentrated sulphuric acid, the curves corresponding closely with those given by pyridinium salts. This is in accordance with Baeyer's formula for the pyroxonium salts (A., 1910, i, 763), the salt formation being represented thus:



Strange to say, the salts of 2:4:6-trimethylpyroxonium have a much greater absorptive power than those of the 4-methoxy-2:6-dimethyl series, that is, the methoxy-group is hypsochromic, and not an auxochrome, in this series. This still further emphasises the analogy between pyroxonium salts and pyridinium salts, for methoxylutidine salts are less absorptive than collidine salts (Purvis, T., 1909, **95**, 295; Baker and Baly, T., 1901, **91**, 1130).

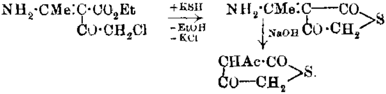
2:6-*Dimethyl*-1:4-*thiopyrone*, $SC{<}^{CH{:}CMe}_{CH{:}CMe}{>}O$, yellow needles, m. p. 145°, is obtained by the action of phosphorus pentasulphide on the corresponding pyrone in benzene. This forms colourless salts with the strong acids, but they are very easily hydrolysed. That the salts contain a free thiol group is shown by the fact that methyl sulphate gives a salt which may be transformed into 2:4:6-*trimethylpyrthionium perchlorate* (annexed formula). The solutions of the thiopyrone in alcohol, water, or chloroform are yellow, but are cherry-red in ether or light petroleum and have different absorption bands. The highly coloured

solutions may possibly contain an isomeride of the annexed formula. The salts have much weaker absorption in concentrated sulphuric acid, and the effect of replacing the ·SH group by the ·SMe group is to displace the bands towards the red. This is remarkable, for the analogous change in the pyrone series, ·OH to ·OMe, is not accompanied by any optical effect.

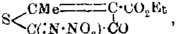


The paper concludes with a criticism of the tendency to formulate all manner of compounds as oxonium salts, for example, the additive compounds of ether with halogen acids, hydroferrocyanic acid, heteropoly-acids, trichloroacetic acid, and even other indifferent substances. J. C. W.

Synthesis of Thiophen Derivatives from Ethyl β-Aminocrotonate. II. ERICH BENARY and L. SILBERSTROM (*Ber.*, 1919, **52**, [*B*], 1605—1613. Compare A., 1915, i, 576).—For some unknown reason, a new supply of 33% potassium hydrosulphide solution has produced from ethyl β-amino-α-chloroacetylcrotonate a compound different to that originally described. The product is apparently *α-acetylthiotetronamide*, for it may be hydrolysed by sodium hydroxide to α-acetylthiotetronic acid (A., 1913, i, 892). It crystallises in long, pale yellow needles, m. p. 233°. The relationships are represented thus:

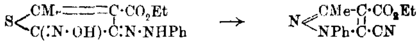


The original product, ethyl 4-hydroxy-2-methylthiophen-3-carboxylate, is always formed if the crotonate is shaken with a suspension of solid potassium hydrosulphide in alcohol. Some further reactions of the ester are now described.

When treated with sodium nitrite in glacial acetic acid, the ester yields *ethyl 3-keto-2-nitroimino-5-methyl-2:3-dihydrothiophen-4-carboxylate*, , which separates in long, yellowish-green needles, decomp. 211°. This behaves as an acid, for it reddens litmus, forms an orange-coloured *compound* with ammonia, $C_8H_8O_5N_2S,NH_3$, which dissolves in water, and gives precipitates of a red *lead* salt, PbX, and a brownish-red *silver* salt, Ag_2X, and also yields a reddish-brown *potassium* salt, K_2X, and a *di*-p-*nitrobenzoyl* derivative, greyish-green tablets, m. p. 162°. The corresponding *3-keto-2-nitroimino-5-methyl-2:3-dihydrothiophen-4-carboxylic acid*, made in the same way from the acid (*loc. cit.*), is a brown powder, decomp. above 100°, which forms a *potassium* salt, K_3X, and an explosive *lead* salt, $(C_6H_3O_6N_2S)_2Pb_3$.

With amyl nitrite, however, the products are the normal oximes.

3-Keto-2-oximino-5-methyl-2 : 3-dihydrothiophen-4-carboxylic acid, $S<\genfrac{}{}{0pt}{}{CMe{=}C\cdot CO_2H}{C(:N\cdot OH)\cdot CO}$, forms green crystals, decomp. 120—130°, and the *ethyl* ester crystallises in pale yellow needles, decomp. 110—130°. The ester yields the nitroimino-compound when treated with sodium nitrite and acetic acid, and gives a dark brownish-red precipitate of a potassium salt when mixed with alcoholic potassium hydroxide. This salt has the colour of permanganate in aqueous solutions, and gives a bright red substance on the addition of acids. The ester also forms a *phenylhydrazone* (*A*), long, white needles, m. p. 152—153°, which is transformed into a pale pink *isomeride*, m. p. 201°, when treated with sodium nitrite and acetic acid, and is converted into *ethyl 5-cyano-1-phenyl-3-methylpyrazole-4-carboxylate* (*B*), white needles, m. p. 88—89°, when boiled with alcohol containing a few drops of hydrochloric acid.



(*A*.) (*B*.)

The ester (*B*) is hydrolysed by boiling alcoholic potassium hydroxide to the corresponding *acid*, soft, felted needles, m. p. 250—251° (*silver* salt), which yields the known 1-phenyl-3-methylpyrazole-4 : 5-dicarboxylic acid (Bülow, A., 1900, i, 56) when boiled with 6% aqueous sodium hydroxide. J. C. W.

The Chemical Constituents of the Bituminous Tar Oils Rich in Sulphur (Ichthyol Oils). III. HELMUTH SCHEIBLER (*Ber.*, 1919, **52**, [*B*], 1903—1910. Compare A., 1916, i, 65; 1917, i, 153).—The purification of an ichthyol oil is effected in three stages. First, it is heated with soda-lime at 170—180° for some hours, the residue from the distillation being decanted, washed with water, and added to the distillate, the whole being then washed with dilute sulphuric acid and dried. By this treatment, the oil loses its obnoxious odour and becomes paler and more mobile. The dry oil is then heated with sodium, a current of ammonia being admitted, and after this treatment it is mixed with magnesium methyl chloride to destroy the small amount of ketone present. A specimen of crude oil from the south of France (500 grams) gave a pleasant-smelling oil (225 grams) containing only carbon, hydrogen, and sulphur, all but the highest fractions being colourless.

Some inconclusive experiments on the behaviour of various fractions of the oil towards mercuric chloride, bromine water, and iodine plus mercuric oxide are described. J. C. W.

Cevine and Sabadinine. KURT HESS and HERMANN MOHR (*Ber.*, 1919, **52**, [*B*], 1984—1988).—Investigation of the alkaloids themselves and of their hydrogen sulphates, potassium salts, aurichlorides, hydrochlorides, and monobenzoyl derivatives shows the

substances to be identical. The formula for the alkaloid is therefore $C_{27}H_{43}O_8N$. Certain corrections of the data recorded in the literature are given. The alkaloid crystallises with $3\cdot5H_2O$, and has m. p. 110°. The hydrogen sulphate $+2\cdot5H_2O$ has m. p. 250° (decomp.), after becoming discoloured at 210°. The potassium salt has the composition $C_{27}H_{41}O_8NK_2$,EtOH, or, more probably,

$$C_{27}H_{42}O_8NK,EtOK.$$

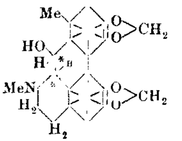
The hydrochloride forms anhydrous needles, m. p. 247°. The aurichloride from sabadinine has m. p. 162° (decomp.), whilst that from cevine has m. p. 167—168° (decomp.). The *monobenzoyl* derivative forms a white, amorphous powder, m. p. 195° (decomp.), after much previous softening. H. W.

Chelidoneum Alkaloids. J. GADAMER (*Arch. Pharm.*, 1919, **257**, 298—303).—Oxidation of the three chelidoneum alkaloids, chelidonine and α- and β-homochelidonines, by means of mercuric acetate indicates that the former two are closely allied and that β-homochelidonine must be placed in the protopine group. Thus, both chelidonine and α-homochelidonine give up two atoms of hydrogen, passing into intensely yellowish-red salts of dehydro-bases which are of quaternary character, but exhibit such a marked tendency to the formation of colourless carbinol bases that they are converted into these even by the action of ammonia. From the fact that the optical activity is considerably increased, it must be assumed that the double linking which is introduced occupies a position adjacent to an asymmetric carbon atom. The optical activity of α-homochelidonine is of the same direction and order of magnitude as that of chelidonine, and the molecule contains, besides the two methoxyl groups, also a methylenedioxy-, a methylimino-, and an alcoholic hydroxyl group. On acylation it behaves similarly to chelidonine; by the action of acetic anhydride at a moderate temperature, acetylation occurs mainly at the oxygen atom (compare Tyrer, *Apoth.-Zeit.*, 1897, 442; Wintgen, A., 1901, i, 743), whilst at the boiling point it takes place almost exclusively at the nitrogen atom with elimination of water and ring-opening (compare Henschke, A., 1889, 62). On *O*-acetylation the optical activity is retained, whilst the *N*-acetyl compound is inactive.

When chelidonine methochloride or methosulphate is boiled with sodium hydroxide solution a strongly lævorotatory methine base and a small proportion of an apparently inactive methine base are formed.

On the basis of these observations, formula I is proposed for chelidonine and formula II for α-homochelidonine, each of these formulæ containing two asymmetric carbon atoms, marked with an asterisk. On oxidation to a didehydro-base, the asymmetry of the carbon atom contiguous to the nitrogen atom disappears, an optically active compound of formula III being obtained. The ring-opening on acetylation at the boiling point must yield first a compound of formula IV, this losing water to form compound V, which

still contains $1H_2O$ more than corresponds with an *N*-acetyl anhydrochelidonine. Further loss of water is, however, less prob



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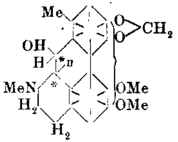

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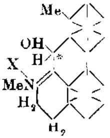

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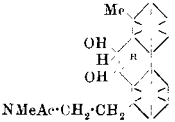

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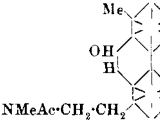
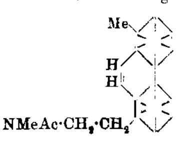


(V.)

able than auto-oxidation and auto-reduction, which should yield a compound of formula VI, but the analytical results do not correspond. The *N*-acetyl derivative is always accompanied by a small proportion of a colourless, quinone-like compound, which gradually turns intensely red and is probably formed by oxidation. These conclusions are supported by the fact that the *O*-acetyl compound cannot be converted into the *N*-acetyl derivative by heating it, either alone or with acetic anhydride.

The lævorotatory methine base obtained by methylation of chelidonine has probably the formula VII. On reduction, didehydrochelidonine is converted into chelidonine and, if the suggested formula is correct, two diastereoisomeric chelidonines should result but their formation has not yet been verified. The free carbinol base must have the structure VIII. The position assumed for the methyl groups is not an entirely arbitrary one, since the alkaloids of the protopine group, which are to be referred to the same components (Bausteine), also contain at this place a side-chain of one carbon atom, this serving likewise to build up a heterocyclic ring.



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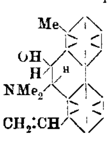

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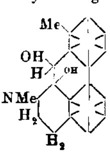

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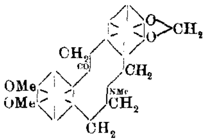

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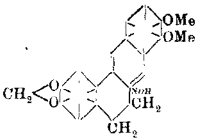

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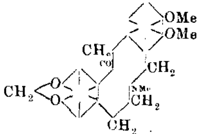

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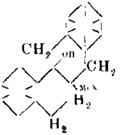


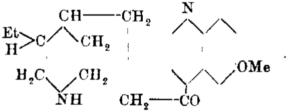
(XII.)

β-Homochelidonine, which resembles protopine and cryptopine in its physiological action, also behaves like these bases towards mercuric acetate; thus, two hydrogen atoms are replaced by an oxygen atom, so that one molecule of the base reduces four molecules of mercuric acetate to mercurous acetate. The product of the oxidation is relatively readily soluble in hot water, giving a slightly alkaline solution. This behaviour and the isomerism of cryptopine and *β*-homochelidonine indicate that the two alkaloids differ only as regards the relative positions of the methylenedioxy- and the two methoxy-groups. Assuming for cryptopine Perkin's formula (IX) (compare T., 1916, **109**, 831), which renders evident its close relationship to berberinium hydroxide (X), *β*-homochelidonine must be represented by formula XI. Confirmation of this formula is furnished (1) by the action of phosphoryl chloride, which yields *iso*-*β*-homochelidonine chloride, identical with dihydroberberine methochloride, and (2) by reduction to dihydro-*β*-homochelidonine and conversion of the latter, by means of phosphoryl chloride, into the chloride of the *iso*-compound, which exhibits complete identity with tetrahydroberberine methochloride.

These results supply a confirmation of Perkin's formulæ for protopine and cryptopine, but an objection to the formulæ for the three bases is the possession of a ten-membered ring, the formation of which in the vegetable organism is as yet unknown. This objection may be removed by the assumption for the salts, which alone are formed in plants, of formula XII. Formula XI or IX would then result only by anhydride formation from the carbinol base produced by the action of alkali. In agreement with this assumption is the fact that, with protopine, cryptopine, and, especially, *β*-homochelidonine, in presence of ammonium chloride, precipitation of the bases by ammonia takes place either not at all or only after some time.

Replacement of the name β-homochelidonine by *allo*cryptopi is recommended. T. H. P.

The Cinchona Alkaloids. XXI. Synthesis of Dihydr quinicine and β-4-Piperidylpropionic Acid. PAUL RABE a KARL KINDLER (*Ber.*, 1919, **52**, [*B*], 1842—1850. Compare A 1919, i, 34).—I. *Synthesis of Dihydroquinicine (Dihydroquin toxine).*—Ethyl quinate and ethyl N-benzoylhomocincholeupona (*ibid.*) are condensed by means of sodium ethoxide in benzene form a β-ketonic ester, which is deprived of the benzoyl and car ethoxyl groups by boiling with 17% hydrochloric acid, thus givi dihydroquinicine,



II. *Synthesis of β-4-Piperidylpropionic Acid.*—4-Methylpyridi is heated with chloral and zinc chloride at 85—90° for sever hours, and thus converted into "γ-*chloralpicoline*" [$\gamma\gamma\gamma$-*trichlor a-4-pyridylpropan-β-ol*], $CCl_3 \cdot CH(OH) \cdot CH_2 \cdot C_5H_4N$, glisteni crystals, m. p. 166° (corr.); *platinichloride*, orange needles, m. 250° (corr., decomp.), *aurichloride*, yellow crystals, m. p. 18 (corr., decomp.). This compound is mixed with ice-cold alcohol potassium hydroxide, and the temperature then allowed to ri when hydrolysis proceeds vigorously, the product being β-4-*pyrid acrylic acid*, $C_5H_4N \cdot CH{:}CH \cdot CO_2H$, pale reddish-brown crysta m. p. 296° (corr., decomp.); *hydrochloride*, $1H_2O$, large, brow crystals, m. p. 243—244° (corr.), *aurichloride*, yellow needles, m. 235° (corr., decomp.). The acid is reduced by sodium in boili amyl alcohol to β-4-*piperidylpropionic acid*,

$$C_5H_{10}N \cdot CH_2 \cdot CH_2 \cdot CO_2H;$$

the acid was not isolated, but converted into the *ethyl* ester, b. 145°/15 mm., *platinichloride*, orange crystals, m. p. 190° (corr decomp.). J. C. W.

Preparation of Nitriles from Quinotoxines. FARBWERK VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 313321; from *Chem Zentr.*, 1919, iv, 499).—Oximinoacidyl derivatives of dihydroquin toxine are treated with acidylating agents in the presence of alkal Reaction occurs in accordance with the scheme:

$$R \cdot C_9H_5N \cdot CO \cdot C(N \cdot OH) \cdot CH_2 \cdot CH{<}{}^{CH_2 - CH_2}_{CHR' \cdot CH_2}{>}N \cdot Acyl \longrightarrow$$

$$R \cdot C_9H_5N \cdot CO_2H + CN \cdot CH_2 \cdot CH{<}{}^{CH_2 - CH_2}_{CHR' \cdot CH_2}{>}N \cdot Ac$$

($R = H$ or OMe; $R' = Et$ or Me.)

Cinchotoxine is converted by benzoyl chloride in the presence

alkali into a *benzoyl* derivative, m. p. 124°, which, when treated with amyl nitrite and sodium alkyloxide, yields a crystalline *oximino*-derivative, m. p. 175—177°; the yellowish-red solution of the latter in sodium hydroxide solution (5%) is transformed by toluene-*p*-sulphonyl chloride at 45° into *benzoylcincholeupono-nitrile*, colourless crystals, m. p. 62°. *Acetylcinchotoxine* is formed as a pale yellow, viscous mass by the treatment of cinchotoxin (quinicine) with acetyl chloride, and, without being further purified, is converted into *oximinoacetylcinchotoxine*, from which *acetylmeroquinenonitrile*, almost colourless, viscous oil, is prepared by the action of benzoyl chloride and sodium hydroxide solution (5%). The nitriles are intended as initial materials for pharmaceutical preparations. H. W.

The Oxidation of Morphine. CONSTANTIN KOLLO (*Bul. Soc. chim. România*, 1919, **1**, 3—9).—Solutions of morphine hydrochloride when sterilised in an autoclave at 120° undergo some decomposition, as shown by the brown colour produced in the liquid. The change occurring is the formation of oxydimorphine (ψ-morphine) and morphine oxide in the proportion of 9 : 1, together with traces of a base said to be methylamine. The percentage of morphine decomposed increases with the temperature to which the solution is heated.

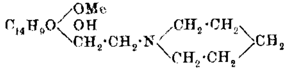
It is suggested that morphine hydrochloride undergoes partial dissociation, and that in the free morphine the group :NMe reacts with the water, giving methylamine and hydrogen peroxide, the latter then acting as an oxidising agent. W. G.

Morphine Alkaloids. VI. The Relative Stability of the Nitrogen Ring in Morphine. JULIUS VON BRAUN (*Ber.*, 1919, **52**, [*B*], 1999—2011).—It has recently been shown (A., 1918, i, 184, 268) that the gradations of stability exhibited by six of the seven classes of bases which have been examined from the point of view of the rupturing of the cyclic system are the same whether the action be effected by Hofmann's method or by cyanogen bromide. Dihydroindole appears to be an exception, since it proves to be one of the most stable systems in the Hofmann degradation, but one of the weakest towards cyanogen bromide. The present communication contains an account of the behaviour of a number of substances containing the grouping, aromatic nucleus, C·C·N, which is present in the morphine molecule. This appears to be extraordinarily resistant to cyanogen bromide, but to be attacked with remarkable ease by bases.

The nomenclature of some of the substances which have been obtained offers certain difficulties, to overcome which the author proposes to designate the group, $C_{14}H_9O(OMe)(OH)\cdot CH_2\cdot CH_2$—, methylmorphimethyl.

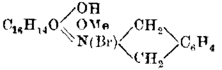
Norcodeinium piperidinium iodide, m. p. 272°, is prepared by the action of norcodeine on αε-di-iodopentane in alcohol, or, preferably, in chloroform (the *platinichloride* is a crystalline powder,

m. p. 215°; the corresponding *dihydronorcodeinium piperidinium iodide* has m. p. 271°), and is converted by cold aqueous sodium hydroxide solution into *methylmorphimethylpiperidine* (annexed formula), stout rods, m. p. 93—94° (the hygroscopic *hydrochloride*, the *platinichloride*, m. p. 174°, the oily *methiodide*, and the *acetyl* derivative, m. p. 87°, are described).



It cannot readily be shown that the disruption of the nitrogen atom has occurred from the morphine and not from the piperidine half of the molecule by the use of acetic anhydride, but the required evidence is readily furnished by the application of cyanogen bromide to the acetyl derivative, which yields *ε-bromoamylcyanoacetylmethylmorphimethylamide*, $C_{14}H_9O(OMe)(OAc)\cdot CH_2\cdot CH_2\cdot N(CN)[CH_2]_5Br$, colourless leaflets, m. p. 133—134°.

Norcodeine and *o*-xylylene bromide similarly yield *norcodeinium-dihydroisoindolium bromide* (annexed formula), long needles, m. p. 262° (*platinichloride*, m. p. 233°), which is transformed by alkali into *methylmorphimethyldihydroisoindole*, m. p. 110°, the salts of which show little tendency to crystallise. The crystalline *acetyl* derivative, shining leaflets, m. p. 146°, yields, however, a *hydrochloride*, colourless leaflets, m. p. 224°, and a *methiodide*, colourless leaflets, m. p. 163°. The course of fission is already established by the nature of the product, and is confirmed by the action of cyanogen bromide on the acetyl derivative, which yields *ω-bromoxylylcyanoacetylmethylmorphimethylamine*, colourless crystals, m. p. 153°.



The interaction of norcodeine and ββ′-di-iodoethyl ether leads to the formation of *norcodeinium-morpholinium iodide*, long needles, m. p. 255—256° (*platinichloride*, m. p. 216°), which is converted by alkali into *methylmorphimethylmorpholine*; since the latter is oily and does not yield well-crystallised salts, it was identified as the *acetyl* derivative, m. p. 118—120° (*platinichloride*, m. p. 177°). Cyanogen bromide transforms the acetyl compound into an oily product, which doubtless consists mainly of the expected bromo-compound, but could not be isolated in the pure state.

H. W.

Ormosine and Ormosinine, Two New Alkaloids from Ormosia dasycarpa. KURT HESS and FRITZ MERCK (*Ber.*, 1919, **52**, [*B*], 1976—1983).—Ormosine has been previously isolated by Merck from *Ormosia dasycarpa*, Jacks, a leguminous plant growing in Venezuela. Its physiological relationship to the morphine alkaloids has been demonstrated by Harnack, but the authors find that it is not allied chemically to these substances, and, indeed,

occupies a unique position among alkaloids. In addition, they have isolated ormosinine from the same source, the yield of the former amounting to 0·15% and of the latter to 0·023% of the dried seeds; these substances, however, only represent a fraction of the total alkaloidal content.

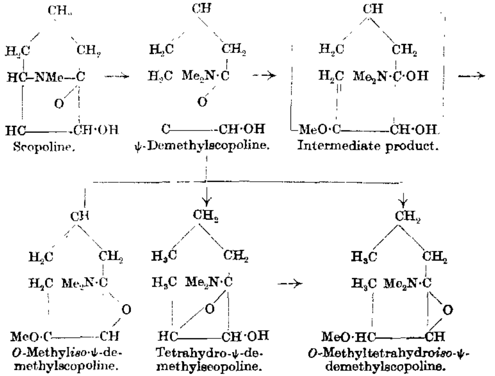
Isolation of the alkaloids is effected by extracting the crushed seeds with alcohol, evaporation of the solvent in a vacuum, and extraction of the residue with water; the aqueous extract is made alkaline with ammonia and extracted with ether. The ethereal solution is shaken with powdered sodium carbonate, after which the solvent is removed, leaving a crystalline residue, from which ormosinine is isolated by taking advantage of its sparing solubility in alcohol, whilst ormosine separates from the alcoholic solution on addition of water.

Ormosine, $C_{20}H_{33}N_3$, crystallises with 3—$4H_2O$ in long needles, m. p. 85—87°, and is readily soluble in alcohol or chloroform. When preserved over sulphuric acid, it loses its water of crystallisation and forms a colourless, gummy mass, which again becomes crystalline when brought into contact with water. It is sensitive towards rise in temperature, and, at 100°, is converted into a viscous oil, which does not recombine with water. With methyl iodide, it gives an abnormally constituted *methiodide*, $C_{24}H_{45}N_3I_2$, long needles, m. p. 245—250° (slow decomp.). The *picrate* has m. p. 178° (decomp.). The *hydrochloride*, *hydrobromide*, and *aurichloride* are amorphous. The *aurichloride* of the *methochloride*, $C_{24}H_{45}N_3Cl_2,2AuCl_3$, forms yellow crystals, which change at 90°.

Ormosinine, $C_{20}H_{33}N_3$, crystallises in well-defined, anhydrous cubes and short prisms, m. p. 203—205°. It yields a normally constituted *methiodide*, $C_{21}H_{36}N_3I$, colourless needles, m. p. 245° (slow decomp.), and a *picrate*, $C_{32}H_{39}O_{14}N_9,4H_2O$. H. W.

Scopoline. IV. Fission of Scopoline by Hofmann's Method of Degradation and Elucidation of the Constitution of Scopoline. KURT HESS (*Ber.*, 1919, **52**, [*B*], 1947—1975).—Previous investigations (A., 1918, i, 404, and previous abstracts) have largely elucidated the constitution of scopoline, leaving in doubt, however, the mode of attachment within the molecule of one valency of one of the oxygen atoms. In the hope of deciding this point, the author has applied Hofmann's method to scopoline. Reaction, however, occurs abnormally, since the product, ψ-demethylscopoline, contains two double bonds, as is evidenced by its ready conversion into a tetrahydro-derivative. Moreover, the process throws no light on the point in question, since the oxygen linking appears to remain intact. When, however, ψ-demethylscopoline is further subjected to the Hofmann degradation, it gives *O*-methyl*iso*-ψ-demethylscopoline, the ammonium base yielding the tertiary amine and methyl alcohol, which adds itself at the ethylene oxide group. Elimination of water occurs from the methylated polyhydroxy-alcohol in such a manner as to form a new ethylene oxide group.

This view is strengthened by the formation of a similarly constituted compound from tetrahydro-ψ-demethylscopoline, which i also produced by the reduction of *O*-methyl*iso*-ψ-demethylscopolin itself. The most ready explanation of these reactions lies in th hypothesis that the ethereal oxygen atom is directly nnited to tha carbon atom to which the nitrogen group is attached, since, if i were attached to one of the other possible carbon atoms, it i difficult to see why the oxygen bridge should be disturbed by a process which only affects the amino-group. The reactions ar consequently shown by the schemes:



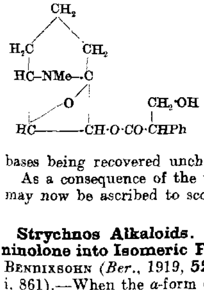
Corresponding with the two asymmetric carbon atoms of ψ-demethylscopoline, the latter is found to exist in two diastereoisomeric racemic forms (α- and β-), both of which have been isolated and used in the series of degradations. During hydrogenation, a third asymmetric carbon atom is developed, so that yet another isomeride is formed.

Scopoline methiodide is converted into the corresponding hydroxide, which is distilled under dimiuished pressure, whereby an oil, b. p. 118—121°/9 mm., is obtained in good yield which consists of a mixture of approximately equal amounts of α- and *β-ψ-demethylscopoline*. The α-form crystallises in needles or prisms, m. p. 67—69° (*picrate*, prismatic needles, m. p. 152—153°; *methiodide*, m. p. 248° [decomp.]; *benzoyl* derivative, indistinct, crystalline needles, m. p. 120°, the *hydrochloride* of which [+3EtOH] has m. p. 214° [decomp.], after much previous softening). The β-form has b. p. 135—140°/15—16 mm. (*picrate*, large, cubic crystals, m. p. 205° [decomp.]; the *methiodide* is oily).

Reduction of *aψ*-demethylscopoline by hydrogen in the presence of colloidal platinum yields a product, b. p. 143—145°/30 mm., which solidifies completely to a mass of long needles, but which is found to be a mixture of two stereoisomerides, since it gives two *picrates*, m. p.'s 182° and 128° respectively, and two *methiodides*, m. p. 209° and oily. The corresponding *β*-base also appears to yield two stereoisomeric *tetrahydro-βψ-demethylscopolines* (b. p. of mixture 135°/27 mm.), the *methiodides* of which are oily. *O-Methyltetrahydro*iso-*aψ-demethylscopoline* is obtained by Hofmann's method from the tetrahydro-*a*-base, and forms an oil, b. p. 122—125°/17 mm., which partly crystallises when preserved, and probably consists of a mixture of isomerides; the *picrate* has m. p. 163°. The corresponding *β*-derivative has b. p. 126—130°/23 mm. (*picrate*, m. p. 183—184°; *platinichloride*, hexagonal crystals, m. p. 200° [decomp.]).

The degradation of *a*- and *β*-*ψ*-demethylscopoline does not occur very smoothly, and in addition to *O-methyl*iso-*aψ-demethylscopoline*, pale yellow oil, b. p. 123°/14 mm., and *O-methyl*iso-*βψ-demethylscopoline*, viscous, yellow oil, b. p. 140°/28 mm., a highly refractive volatile *oil*, $C_7H_8O_2$, of characteristic odour, b. p. 88—92°/11 mm., is obtained. A *picrate*, needles, m. p. 142—143°, was isolated from the product of the degradation of the mixed bases.

The oxygen bridge in *aψ*-demethylscopoline, unlike that in scopoline itself (A., 1916, i, 286), does not appear to be opened by treatment with hydrogen bromide in glacial acetic acid solution, the products of the action being the *hydrobromide* of the original base, prisms, m. p. 250° (decomp.), and resinous matter.



Attempts further to degrade the tetrahydro-*O*-methyl*iso*-*ψ*-demethylscopolines were unsuccessful, the bases being recovered unchanged.

As a consequence of the work on scopoline, the annexed formula may now be ascribed to scopolamine. H. W.

Strychnos Alkaloids. XXV. Rearrangement of Strychninolone into Isomeric Forms. HERMANN LEUCHS and WALTER BENDIXSOHN (*Ber.*, 1919, **52**, [*B*], 1443—1453. Compare A., 1914, i, 861).—When the *a*-form of strychninolone, $C_{19}H_{18}O_3N_2$, is shaken with 0·5*N*-sodium hydroxide for a few days, about 80% of it is changed into strychninolone-*b*, massive crystals, m. p. 228°, $[\alpha]_D^{20}$ −37·3°. The alkali contains about 6% of the by-product, $C_{19}H_{20}O_4N_2$, m. p. 235—270°, $[\alpha]_D^{20}$ +21·5°, which was also formed during the fission of strychninolic acid. A similar transformation is effected by heating the *a*-form with methyl-alcoholic ammonia in a sealed tube. The products are the *b*-form, a new isomeride which is less soluble in methyl alcohol, namely, *strychninolone-c*, hexagonal prisms or pointed and twinned leaflets, m. p. 251—252°,

$[\alpha]_D^{12}$ −176·1°, and two isomeric amines. These are *aminodihydrostrychninolone*-I, $C_{19}H_{21}O_3N_3,H_2O$, polyhedric tablets or columns, m. p. 185—191° (decomp.), which forms a sparingly soluble *nitrate*, m. p. 261—263° (decomp.), $[\alpha]_D^{15}$ −51·6°, and a *phenylcarbamide*, $C_{26}H_{26}O_4N_4$, m. p. 240—241°, and again at 295—300°, and also *aminodihydrostrychninolone*-II, stout needles, m. p. 236—239° (decomp.), $[\alpha]_D^{14}$ −66·6°, which forms a soluble nitrate.

When strychninolone-*b* is covered with 12*N*-hydrochloric acid, it changes into the salt of an *amino-acid*, $C_{19}H_{20}O_4N_2,4H_2O$, broad needles, m. p. 239—240° (decomp.), which is identical with the strychninolone-hydrate-II, already described (A., 1910, i, 768). Strychninolone-*b* also forms an *acetate*, $C_{21}H_{20}O_4N_2$, when heated with acetic anhydride and sodium acetate. This crystallises in prisms with 1MeOH, m. p. 140° (decomp.), and then 214°, $[\alpha]_D^{20}$ −37·6°, and may be formed by heating acetylstrychninolone-*a* with acetic anhydride. J. C. W.

Strychnos Alkaloids. XXVI. Degradation of Bromostrychnine and Dihydrostrychninonic Acid, and the Bromination of the Fission Products of Strychnine. HERMANN LEUCHS and DOROTHEA RITTER (*Ber.*, 1919, **52**, [*B*], 1583—1593).

Bromostrychnine (Beckurts, A., 1885, 911) is most conveniently made by adding bromine water to strychnine dissolved in hydrobromic acid, for it separates as the hydrobromide (solubility at 15°, 1%), leaving the salt of the unchanged base in solution. When oxidised by permanganate at −10° to 15° in acetone solution, it yields bromostrychninonic acid (soluble in chloroform; A., 1910, i, 766) and insoluble *bromodihydrostrychninonic acid*,

$C_{21}H_{21}O_6N_2Br$.

This crystallises in minute, hexagonal leaflets, m. p. 310° (decomp.), $[\alpha]_D^{20}$ −19·7° (in 0·1*N*-sodium hydroxide), may also be obtained by brominating dihydrostrychninonic acid, and is gradually hydrolysed by *N*-alkali hydroxide in the cold to glycollic acid and a *compound*, $C_{19}H_{17}O_3N_2Br$, which crystallises from alcohol in slender needles, m. p. 273°, $[\alpha]_D^{20}$ −24·2°.

Dihydrostrychninonic acid, obtained in 6% yield by oxidising strychnine with permanganate in boiling acetone, is hydrolysed by *N*-alkali hydroxide to two isomerides, according to the conditions. In the cold, the product is *isostrychninolone*-I, $C_{19}H_{18}O_3N_2$, colourless pyramids, m. p. 246—247°, $[\alpha]_D^{20}$ +46·4°, which yields the above compound, $C_{19}H_{17}O_3N_2Br$, on bromination. At 100°, the product is *isostrychninolone*-II, long, woolly needles, not molten at 310°, $[\alpha]_D^{20}$ −126°, giving a cornflower-blue colour with chromic and sulphuric acids, and a very sparingly soluble *bromo*-derivative, m. p. 280°.

Strychninonic acid yields the same acid on bromination as bromostrychnine gives on oxidation, namely, bromostrychninonic acid. The *methyl* ester of this, $C_{22}H_{21}O_6N_2Br$, has m. p. 230—231°, and the *ethyl* ester, m. p. 247° (corr.). The acid is reduced by sodium amalgam to *bromostrychninolic acid*, $C_{21}H_{21}O_6N_2Br$, minute prisms,

lecomp. 265—270°, which is gradually hydrolysed by N-sodium ıydroxide to glycollic acid and bromostrychninolone-*a* (below).

The *a*- and *b*-forms of strychninolone yield on bromination *ıromostrychninolone*-a, $C_{19}H_{17}O_3N_2Br$, stout tablets, m. p. !54—256°, $[\alpha]_D^{20}$ −62·2°, and *bromostrychninolone*-b, stout prisms ır tablets, m. p. 233—235°, $[\alpha]_D^{20}$ −72·8°. J. C. W.

Synthesis of 2-*n*-Butylpyrrolidine. Remarks on the Vork of E. Blaise and Houillon on the Transformation of he Higher Alkylenediamines into Cyclic Mono-imines. ꞰURT HESS (*Ber.*, 1919, **52**, [*B*], 1636—1641).—2-Pyrryl propyl .etone (Oddo, A., 1910, i, 426) is reduced by sodium and alcohol o α-2-pyrrolidylbutyl alcohol (A., 1916, i, 68), the constitution of ·hich has been proved (A., 1917, i, 351, 352), and this is ıeated with hydriodic acid (D 2·0) and red phosphorus at 25—135°. *2-n-Butylpyrrolidine* is a colourless oil, b. p. 54—156°/753 mm., which has a very similar odour to coniine, and ˢ only sparingly soluble in water. The *platinichloride* forms tout prisms, m. p. 178°, and the *aurichloride* is an unstable, egg-ellow, flocculent powder, m. p. 145°. When heated with formaldeyde and formic acid, the base yields *1-methyl-2-n-butylpyrrolidine*, . p. 154—155°/15 mm., which forms a *platinichloride*, long, ırismatic tablets, m. p. 215°, and an *aurichloride*, m. p. 190°.

The base described by Blaise and Houillon as 2-*n*-butylpyrrolidine (A., 1906, i, 692) must have had some other constitution.

J. C. W.

Pyrrolidine Derivatives. V. Preparation of the Three Iydroxyprolines which are Stereoisomerides of the Natural Hydroxyproline. HERMANN LEUCHS and KARL BORMANN *Ber.*, 1919, **52**, [*B*], 2086—2097).—The work is a continuation of hat described previously (Leuchs and Brewster, A., 1913, i, 449).

dl-Hydroxyproline (*a*) is resolved by crystallisation of the ıuinine salt of its phenylcarbamide, as described previously; the pecific rotation of the synthetic *l*-hydroxyproline (*a*) in aqueous olution cannot be raised above −75·7°, a value which agrees well ·ith that recorded previously, but is lower than the sole datum −81°) for the natural acid. *d-γ-Hydroxyprolinephenylcarbamide* *a*) has m. p. 175°, $[\alpha]_D^{27}$ +37° (in water as ammonium salt); *l-hydroxyproline* (*a*) has m. p. about 274°, $[\alpha]_D^{22}$ +75·2° in aqueous olution. The corresponding *hydantoin* has m. p. 130—131° anhydrous), ca. 70° (+$2H_2O$), $[\alpha]_D^{23}$ +49·2°, for the anhydrous subtance in water.

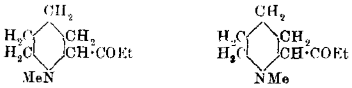
dl-γ-Hydroxyprolinephenylcarbamide (*b*) is similarly resolved ıy means of quinine, as previously described; *l*- and *d*-hydroxyıroline (*b*) have now been obtained in the crystalline form, slender ıeedles, m. p. 238—241° (decomp.), $[\alpha]_D^{18}$ −58·1° and +58·6° espectively.

The product obtained by racemising the natural hydroxyproline vith barium hydroxide appears to be identical with that obtained

by mixing equal weights of *l*-hydroxyproline (*a*) and *d*-hydroxyproline (*b*); it appears that a change of configuration only occurs at the α-carbon atom, whilst the γ-carbon atom remains unaffected.

Derivatives of *dl*-hydroxyproline (*a*) and (*b*) with phenylthiocarbimide are described, but are unsuitable for purposes of resolution owing to the ease with which they pass into anhydrides which are either thiohydantoins or thioazlactones; γ-*hydroxyprolinephenylthiocarbamide* forms nodular crystals, and when crystallised from warm water or heated at 63° readily gives the corresponding *anhydride*, slender needles, m. p. 145—148°; its m. p. is the same as that of the anhydride; γ-*hydroxyprolinephenylthiocarbimide* (*b*), m. p. 155—156°, is rather more stable than the α-derivative. The corresponding *anhydride* crystallises in small needles, m. p. 146—148°. H. W.

The Asymmetric, Tervalent Nitrogen Atom. II. New Transformations of *dl*-Methylconhydrinone and the Conversion of *d*-Conhydrinone into *dl*-α-2-Pyrrolidylbutan-β-one. KURT HESS (*Ber.*, 1919, **52**, [*B*], 1622—1636. Compare A., 1919, i, 345).—In the former paper, it was shown that α-1-methyl-2-piperidylpropan-α-one exists in two stereoisomeric forms, methyl*iso*pelletierine (I) and methylconhydrinone (II).



(I.) (II.)

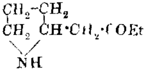
A further proof of the close relationship between these bases is now given, namely, the fact that when their hydrazones are boiled with sodium ethoxide solution they both yield *dl*-methylconiine.

In the further elucidation of this unusual case of isomerism, it is found that during changes at the asymmetric nitrogen atom, the particular configuration is preserved, but that changes at the propyl residue, that is, at the asymmetric carbon atom, lead to the same products in both cases.

As a reaction of the former type may be mentioned the dimethylation by means of ethyl azodicarboxylate. This leads to the production of *iso*pelletierine on the one hand and dl-*conhydrinone*, b. p. 93—94°/10 mm., on the other. Furthermore, the ethylurethane of *d*-conhydrinone (*loc. cit.*) is isomeric with the *ethylurethane* of *iso*pelletierine, this having now been obtained as a viscous oil, b. p. 165—170°/13 mm., by the action of ethyl chloroformate on the base in ether, under the influence of powdered potassium carbonate.

A most remarkable difference between these isomeric ethylurethanes is described. When boiled with aqueous-alcoholic sodium hydroxide, the *iso*pelletierine derivative is slowly hydrolysed to *iso*pelletierine and resinous products, whereas the *d*-conhydrinone

derivative is quickly and almost quantitatively converted into dl-α-2-*pyrrolidylbutan-β-one* (annexed formula). This oil has b. p. 95—97°/10 mm., responds readily to the pine-shaving test, forms a *picrate*, bundles of needles, m. p. 155°, is converted by heating with formaldehyde and formic acid into α-1-*methyl*-2-*pyrrolidylbutan-β-one*, b. p. 112—115°/22 mm. (*hydrochloride*, m. p. 153°; *platinichloride*, m. p. 205°; *methiodide*, long spikes, m. p. 213—215°), and yields a *hydrazone*, b. p. 135—140°/15 mm., which is reduced by heating with sodium ethoxide solution at 150—170° to 2-butylpyrrolidine (see this vol., p. 85). J. C. W.

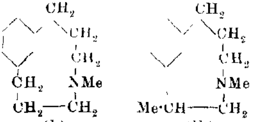


Additive Compounds of Acyl Chlorides and Tertiary Amines. KARL FREUDENBERG and DANIEL PETERS (*Ber.*, 1919, **52**, [*B*], 1463—1468).—In many cases, chloroform is an excellent medium in which to study reactions between acyl chlorides and tertiary amines, *for the additive compounds readily separate*, leaving such by-products as the amine hydrochlorides and dehydracetic acid in solution, and, furthermore, there is much less danger of the precipitate absorbing atmospheric moisture during filtration than when ether is used as the diluent (compare Dehn, A., 1912, i, 833; 1914, i, 1169). The true additive compounds are extremely sensitive to water and alcohol, especially in those cases in which intermolecular expulsion of hydrogen chloride is possible, and this is why so few genuine compounds of this type have been described.

Oxalyl chloride and pyridine form a compound in the ratio 1 : 2 (Jones and Tasker, P., 1908, **24**, 271), which separates in yellow, sandy crystals and evolves carbon monoxide and dioxide on exposure to moist air. Acetyl chloride and pyridine unite in the ratio 1 : 1 (Dennstedt and Zimmerman, A., 1886, 368), the compound dissolves in the chloroform if moisture is allowed to enter, and reacts with alcohol to form pyridine hydrochloride and ethyl acetate. The compound given by hexamethylenetetramine and benzoyl chloride is also decomposed by alcohol, which Hartung overlooked when he spoke of it as being somewhat soluble in this medium (A., 1892, 1173). J. C. W.

Ring Closure in the Meta-position in the Benzene Series. I. Reduction of Julolidine Methochloride. JULIUS VON BRAUN and LUDWIG NEUMANN (*Ber.*, 1919, **52**, [*B*], 2015—2019). —It has been shown previously (von Braun, Heider, and Wyczatkowska, A., 1919, i, 40) that the reduction of julolidine methochloride by sodium amalgam leads to the formation of a base, $C_{13}H_{19}N$. The latter has now been isolated as a colourless oil, b. p. 87—89°/0·01 mm., which can be preserved unchanged in a closed vessel (the methiodide has m. p. 178° instead of 200°, as previously recorded). When this is converted into its methiodide, treated with silver oxide, and the product is distilled under greatly

diminished pressure, two fractions are obtained: (1) unchanged base mixed with a certain amount of an unsaturated base, and (2) an oxy-*base*, $C_{14}H_{23}ON$, syrupy liquid, b. p. 145—147°/0·01 mm. The *hydrochloride*, *platinichloride*, *picrate*, and *methiodide* of the latter are oily, but the *platinum* salt of the methochloride forms orange needles, m. p. 165°. The nitrogen atom of the base, like that of the original amine, is not attached to the aromatic nucleus, neither is oxygen present as phenolic hydroxyl. In confirmation of these facts, it is found that only *iso*phthalic acid is formed when it is oxidised. It follows, therefore, that the base $C_{13}H_{19}N$ must contain the complex $C_6H_{12}NMe$ in the form of a closed chain united to two carbon atoms of the benzene nucleus which are in the meta-position to one another. The structure of the complex can be deduced with considerable probability from the following facts: (1) the nitrogen is probably in the γ-position to the benzene nucleus, since attempts to apply Hofmann's process to the degradation of the oxy-base were unsuccessful, and (2) the production of a tertiary hydroxy-amine instead of an unsaturated amine in Hofmann's reaction is only probable if a primary alcoholic group can be developed. The grouping $-CH_2·CH_2·CH_2·NMe·CH_2-$ is therefore probably present in the amine, $C_{13}H_{19}N$, and the annexed formulæ are thus possible. The second of these is, however, very improbable, since the corresponding hydroxy-base would show a great tendency to eliminate water and form a methylated styrene complex, and since, also, α-methyl-lilolidine, which is very analogously constituted to julolidine, does not yield a trace of a base analogous to $C_{13}H_{19}N$ when its methochloride is reduced. H. W.



(I.) (II.)

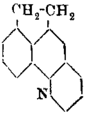
The Acetyl Derivative of β-Indoxylcinnamic Acid. Rud. Wegscheider (*Ber.*, 1919, **52**, [*B*], 1705).—The acetyl derivative obtained by Scholtz (A., 1919, i, 96) may be represented by the formula $\underset{NH—CH·CPh:CH·CO}{C_6H_4·C(OAc)——O}$. J. C. W.

Modification of Skraup's Synthesis for Preparing Quinoline Bases: their Conversion into Stannichlorides. J. G. F. Druce (*Chem. News*, 1919, **119**, 271—273).—The method adopted for the synthesis of quinoline from aniline stannichloride (A., 1918, i, 535) has been applied successfully, although with diminished yields, to the synthesis of homologues of quinoline. Thus *o*-, *m*-, and *p*-toluidine stannichlorides treated with glycerol and sulphuric acid heated at 120° for two to three hours and then diluted and diazotised gave, respectively, 8-, 7-, and 6-methylquinoline in yields varying from 25% with the meta- to 70% with the para-compound.

On the other hand, *m*- and *p*-phenylenediamine stannichlorides gave extremely poor yields of the phenanthrolines. The stannichlorides of the methylquinolines were prepared by dissolving crystalline stannic chloride in hydrochloric acid solutions of the bases, and they crystallised out on cooling. 6-*Methylquinoline stannichloride* forms white plates, m. p. 248°, 7-*methylquinoline stannichloride*, pale yellow needles, m. p. 229°, and 8-*methylquinoline stannichloride*, white needles, m. p. 252° (with decomp.). m-*Toluidine stannichloride*, prepared in an analogous fashion, formed pearly-white plates, soluble in cold water and alcohol, m. p. 76°. *m*-Toluidine stannichloride crystallised in pale pink, nacreous plates, m p. 284°. A rapid method for the estimation of chlorine in these and other tin salts of aliphatic and aromatic bases was devised, consisting in simple titration with *N*/10-sodium hydroxide, using phenolphthalein as indicator. Good results were obtained with aromatic compounds, but the stronger alkalinity of the aliphatic bases interferes with the end-point to some extent, and less accurate results are consequently obtained. G. F. M.

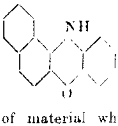
Preparation of Indigoid Dyes. ADOLF JOLLES (D.R.-P. 305558; from *Chem. Zentr.*, *1919*, iv, *619*).—Aromatic hydroxy-derivatives containing a phenolic hydroxyl group are oxidised in the presence of indoxyl or indoxylic acid. Thus a mixture of "2-*naphthalene*-2-*indolindigo*" and "4-*naphthalene*-2-*indoleindolignone*" (separable by extracting the latter with boiling dilute sodium hydroxide solution) is obtained when indoxyl and α-naphthol dissolved in acetic acid are oxidised by a solution of ferric chloride in hydrochloric acid. A solution of the 20% indoxylic acid fusion and α-anthrol, when similarly treated, yields "2-anthracene-2-indolindigo" (identical with the dye prepared from isatin-α-anilide and α-anthrol). H. W.

Synthesis of 2 : 3-Pyridinoacenaphthene. ALOIS ZINKE and EMMY RAITH (*Monatsh.*, 1919, **40**, 271—276).—The experiments were undertaken with the object of ultimately preparing an α-naphthaquinoline-6 : 7-dicarboxylic acid; the anhydride of such an acid is described, but the yields are not sufficiently satisfactory to permit further work.

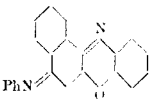


2 : 3-*Pyridinoacenaphthene* (annexed formula), colourless, ice-like crystals, m. p. 67° (uncorr.), is obtained by the action of concentrated sulphuric acid, glycerol, and nitrobenzene on 3-aminoacenaphthene. The *hydrochloride*, long, pale yellow needles, m. p. 305°, the *sulphate*, small, yellow needles, m. p. 238°, and the *methiodide*, yellow needles united in clusters, which does not melt below 315°, are described. Oxidation of the base or of its salts by chromic acid in acetic acid solution leads to the formation of α-naphthaquinoline-6 : 7-dicarboxylic anhydride, long, red needles, m. p. 317°. H. W.

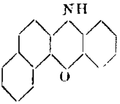
1 : 2-Naphthaphenazoxines. HENRI GOLDSTEIN and ZDENKA LUDWIG-SEMELITCH (*Helv. Chim. Acta*, 1919, **2**, 655—662. Compare Kehrmann and Neil, A., 1915, i, 303).—1 : 2-α-*Naphthaphenazoxine* (annexed formula),



yellow solid, m. p. 107° (decomp.), is prepared by gradually heating a mixture of α-amino-β-naphthol hydrochloride and *o*-aminophenol to 260° in a current of carbon dioxide; it is a very unstable substance which cannot be purified by crystallisation, the physical properties recorded being those of a small amount of material which had sublimed during the preparation. The *acetyl* and *benzoyl* derivatives could not be obtained in the crystalline state. The composition of the substance is deduced from the conversion of the crude product into naphthaphenazoxone, on the one hand, and into 6-*phenylnaphthaphenoxazime* (annexed formula) on the other.



The constitution of the latter substance is established by its synthesis from *o*-aminophenol hydrochloride and anilino-β-naphthaquinone; it forms orange needles, m. p. 215°, and behaves as a very weak base. The *hydrochloride*, slender, red needles with green reflex, and the *platinichloride*, small, brown crystals, are described.



1 : 2-β-*Naphthaphenazoxine* (annexed formula) is formed, together with the α-isomeride, by heating a mixture of αβ-dihydroxynaphthalene and *o*-aminophenol. It forms yellow crystals, which darken in the air at about 110° and melt in a closed tube at 127—128°. The *acetyl* derivative could not be caused to crystallise. It is converted by aniline hydrochloride and ferric chloride into 3-*phenyl*iso*naphthaphenoxazime*, which is a weak, unstable base; the *hydrochloride* and *platinichloride* are described.

H. W.

Stereochemistry of Rhodanines. II. STEN KALLENBERG (*Ber.*, 1919, **52**, [*B*], 2057—2071. Compare A., 1917, i, 279).—It is found that rhodanines with a tertiary β-carbon system and such as contain the asymmetric carbon atom outside the thiazole ring exhibit normal properties, and can be obtained in stable active forms. Rhodanines in which a hydrogen atom is united to the asymmetric β-carbon atom cannot be isolated in the active state. The most obvious explanation is to regard them as thiazolines (II) instead of thiazolidines (I), although it is also possible that a keto-enolic equilibrium is set up.

$$NR<\begin{matrix}CO\cdot CHR' \\ CS\cdot S\end{matrix} \qquad NR<\begin{matrix}C(OH):CR' \\ CS——S\end{matrix}$$

(I.) (II.)

The condensation of *d*-thiolactic acid and phenylthiocarbimide

leads to the formation of *r*-3-phenyl-5-methylrhodanine, m. p. 114—116°.

5-*Methyl-3-ethylrhodanine*-5-*acetic acid*,

$$NEt<\begin{matrix}CO\cdot CMe\cdot CH_2\cdot CO_2H \\ CS\text{—}S\end{matrix},$$

is prepared by the condensation of sodium *l*-methylbromosuccinate on potassium ethyldithiocarbamate in aqueous solution; it separates from water in long, pale yellow needles, m. p. 73—75° (+1H_2O), 107—109° (anhydrous), $[\alpha]_D$ −54·4° in alcoholic solution (for hydrated acid). The corresponding d-*isomeride* has m. p. 73—75°, $[\alpha]_D$ +55·5°, and is optically stable towards barium hydroxide solution at the ordinary temperature. The *r*-acid forms thin, colourless, anhydrous leaflets, m. p. 108—110°.

It has been shown by Holmberg (A., 1912, i. 131) that trithiocarbodiglycollic acid condenses with *r*-β-phenylethylamine to yield 3-β-phenylethylrhodanine; if the action is carried out with the optically active bases, however, the active diphenylethylthiocarbamides, needles, m. p. 195—197°, $[\alpha]_D$ −13·5° and +14·1° in alcoholic solution, are produced, identical with the products described by Lovén and Ohlsson (A., 1914, i, 830). The active 3-phenylethylrhodanines may, however, be prepared as follows. *d*-Phenylethylamine is treated successively with aqueous potassium hydroxide solution and carbon disulphide and with an aqueous solution of sodium chloroacetate, whereby d-*phenylethyldithiocarbamineglycollic acid*, colourless, crystalline powder, m. p. 101—102°, $[\alpha]_D$ +120·4° in alcoholic solution, is produced, which, when gently warmed with dilute acetic acid, loses water and passes into d-3-*phenylethylrhodanine*, pale yellow needles, m. p. 108—109°, $[\alpha]_D$ +301·2° in alcoholic solution. l-*Phenylethyldithiocarbamineglycollic acid* has m. p. 101—102°, $[\alpha]_D$ −121·0° in alcohol, whilst l-3-*phenylethylrhodanine* has m. p. 108—109°, $[\alpha]_D$ −304·8°. The corresponding *r*-acid and *r*-rhodanine have m. p.'s 104—106° and 110—111° respectively. The latter is converted by a solution of sodium in alcohol into the *substance*, $CHMePh\cdot N<\begin{matrix}C(SH)(OEt) \\ CO\text{——}CH_2\end{matrix}>S$, small, pale red prisms, m. p. 93—94°, which could only be isolated in one of two possible stereoisomeric forms.

r-3-*Ethylrhodanine*-5-*acetic acid*, small, pale yellow needles, m. p. 118—119°, is obtained by the action of potassium ethyldithiocarbamate on sodium *l*-bromosuccinate in aqueous solution, racemisation being complete. The *sodium hydrogen* salt, greenish-yellow plates, m. p. 242—243° (decomp.), is described.

The possibility of obtaining optically active products from salts of *l*-bromosuccinic acid and dithiocarbamates is established by experiments with diethyldithiocarbamates; when the substances are allowed to react in dilute aqueous solution, l-*diethyldithiocarbaminemalic acid*, $CO_2H\cdot CH_2\cdot CH(CO_2H)\cdot S\cdot CS\cdot NEt_2$, m. p. 106—107°, $[\alpha]_D$ −6·67° in alcohol, −40·9° in ethyl acetate, is obtained, which is probably not optically pure and is completely racemised in boil-

ing aqueous solutions. When the condensation is effected in mor concentrated solution, complete racemisation occurs, and the corre sponding *r*-acid, m. p. 114—116°, is formed, which is also produce by the action of *r*-bromosuccinic acid on potassium diethyldithio carbamate.

Sodium *l*-β-bromosuccinamate condenses with potassium dimethy dithiocarbamate in aqueous solution to yield l-*dimethyldithiocarb amylsuccinamic acid*, colourless, silky needles, m. p. 158—159° (th sodium salt has $[\alpha]_D$ −4·2° in aqueous solution), which, in hot aci solution, passes into r-*dimethyldithiocarbamylsuccinic acid*, smal rhombic plates, m. p. 145—146°, and in alkaline solution extensively decomposed with formation of the half-amide of fumar acid. The acid is oxidised by permanganate to d-*dimethylthiocarb amylsuccinamic acid*, m. p. 148—149°, $[\alpha]_D$ +80·5° in alcohol solution. r-*Dimethyldithiocarbamylsuccinamic acid*, small, colour less prisms, m. p. 162—163° (decomp.), is similarly prepared fro *r*-β-iodosuccinamic acid, and is similarly oxidised to r-*dimethylthi carbamylsuccinamic acid*, colourless prisms, m. p. 153—154 (decomp.). A similar series of reactions yields d-*phenylmethy dithiocarbamylsuccinamic acid*, small, colourless prisms, m. p 164—165° (decomp.), $[\alpha]_D$ +11·0° in acetone (*ammonium* sal colourless needles; *sodium* salt, small, colourless needles; *potassiu* salt, colourless leaflets). The acid is converted into the r-*este* small, colourless, rhombic plates, m. p. 135—136°, by ethyl alcoh and hydrogen chloride. In hot acid solution it is transformed int r-*phenylmethyldithiocarbamylsuccinic acid*, m. p. 163—164°, an in alkaline solution it is extensively decomposed, yielding, amongs other products, the half-amide of fumaric acid. It is oxidised b permanganate to d-*phenylmethylthiocarbamylsuccinamic aci* colourless, rhombic plates, m. p. 168° (decomp.), $[\alpha]_D$ +63·9° i alcohol. r-*Phenylmethyldithiocarbamylsuccinamic acid* form colourless, rhombic plates, m. p. 157—158° (decomp.), and i oxidised to r-*phenylmethylthiocarbamylsuccinamic acid*, prism m. p. 160—161° (decomp.). H. W.

3 : 3′-Dimethyl-6 : 6′-di*iso*propylbenzidine. C. E. Andrew (U.S. Pat. 1314924).—Symmetrical dimethyldi*iso*propylbenzidine i produced by reducing crude mononitrocymene (such as may b obtained from "spruce turpentine") in alkaline solution to form hydrazocymene, subjecting the latter to the "benzidine transform ation," and purifying the product by precipitation as sulphate The sulphate is a white, crystalline powder which is easily separate by filtration, the impurities remaining in solution. The sulphat is decomposed on addition of a 10% sodium hydroxide solution with liberation of the free base, dimethyldi*iso*propylbenzidine. Th r is an oily liquid, b. p. about 250°. It may be employed in eparation of azo-dyes. CHEMICAL ABSTRACTS.

tic Analogues of Novocaine. Julius von Braun and The cond Schdaum (*Ber.*, 1919, **52**, [*B*], 2011—2015).—It has

recently been shown by Fränkel and Cornelius (A., 1919, i, 66) that derivatives of primary β-aminoethyl alcohol, in contrast to the tertiary *N*-dialkylated alkamine derivatives (stovaine, novocaine), do not possess anæsthetising action. The compounds which they have examined, however, contain an acyl residue attached to the nitrogen atom in place of the alkyl radicle of novocaine, and thus do not belong to quite the same type. Closer analogy is shown by a series of substances, which are now described, and in which a phenyl or substituted phenyl group is introduced in place of one of the alkyl groups. It is found that the aromatic substitution at the nitrogen atom of novocaine is without influence on its anæsthetising power if the basicity of the molecule is also suitably increased.

N-β-*Benzoyloxyethyl*-N-*methyl*-p-*phenylenediamine*,

$NH_2\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CH_2\cdot OBz$,

long, slender needles, m. p. 56° (the *hydrochloride* and *acetyl* lerivative, m. p. 152°, are described), is obtained by the reduction of the corresponding p-*nitroso*-derivative, pale green powder, m. p.)0°. Sodium *p*-nitrobenzoate reacts readily with β-chloro- or nethyl-β-bromo-ethylaniline, yielding N-β-p-*nitrobenzoyloxy-thyl*-N-*methylaniline*, $NMePh\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$, *yellow* ieedles, m. p. 70° (*hydrochloride*, colourless substance, *picrate*, n. p. 177°, *methiodide*, m. p. 144° [decomp.]), which is reduced to N-p-*aminobenzoyloxyethyl*-N-*methylaniline*, colourless leaflets, m. p. 12° (*acetyl* derivative, m. p. 132°). When the solution of the atter in dilute hydrochloric acid is treated with sodium nitrite, it rields the corresponding p-*nitroso*-derivative, m. p. 105—106°, vhich is almost quantitatively reduced by stannous chloride to N-β-p-*aminobenzoyloxyethyl*-N-*methyl*-p-*phenylenediamine*,

$NH_2\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot NH_2$,

n. p. 98°; the *hydrochloride* of the latter is freely soluble in water; he *diacetyl* derivative has m. p. 146°. Sodium 3:5-dinitro-enzoate and methylchloroethylaniline yield N-β-3:5-*dinitrobenzoyl-xyethylmethylaniline*, m. p. 121°, which is normally reduced to the orresponding *diamino*-compound, m. p. 80°, the *hydrochloride* of vhich is very hygroscopic. H. W.

Action of Basic Reagents on Schiff's Bases. I. The Chloralnitroaniline Group. A. S. WHEELER and S. C. SMITH (*J. Amer. Chem. Soc.*, 1919, **41**, 1862—1865).—Schiff's bases, btained by condensing *o*- and *p*-nitroaniline with chloral (compare Vheeler and Weller, A., 1903, i, 246), yield hydroxy-, methoxy-, nd ethoxy-derivatives with alcoholic potassium hydroxide, sodium iethoxide, and sodium ethoxide; in each case, one chlorine atom s replaced. The *m*-nitroaniline–chloral product is so sensitive to hese basic reagents that each of them in the cold breaks it up into s constituents. The nitro-group in the benzene ring of the amine tabilises the Schiff's bases to such an extent that basic reagents ield derivatives, although this is not true when it is in the meta-osition. The following new substances are described: NN′-βββ-*di-*

chlorohydroxyethylidenebis-o-nitroaniline,

$$OH\cdot CCl_2\cdot CH(NH\cdot C_6H_4\cdot NO_2)_2,$$

brilliant yellow prisms, m. p. 143°; NN′-ββ*β-dichloromethoxyethylidenebis-o-nitroaniline*, yellow, rectangular plates, m. p. 147°; NN′-ββ*β-dichloroethoxyethylidenebis-o-nitroaniline*, brilliant yellow, rectangular plates, m. p. 135°; NN′-ββ*β-dichloroethoxyethylidenebis-p-nitroaniline*, bright yellow, fan-shaped crystals, m. p. 147°.

H. W.

Constitution of Triphenylmethane Dyes. HUGO KAUFFMANN (*Ber.*, 1919, **52**, [*B*], 1421—1422).—One of the most puzzling facts in connexion with the constitution of triphenylmethane dyes is the hypsochromic effect of the introduction of a third amino-group in such compounds as malachite-green (Hantzsch, A., 1919, ii, 255). This can only be explained on electrochemical lines, as developed by the author in his theory of valency subdivision (this vol., i, 50). A compound containing two methoxyl auxochromes in the third benzene nucleus of malachite-green has now been obtained by converting Michler's ketone into the chloride with phosphoryl chloride and condensing this with *m*-dimethoxybenzene under the influence of aluminium chloride. 4:4′-*Tetramethyldiamino-2″:4″-dimethoxytriphenylcarbinol* is white, has m. p. 195°, and dissolves in acids with the following colours: dilute acetic acid, bluish-green; dilute mineral acids, red becoming bluish-green on dilution; concentrated sulphuric acid, orange.

J. C. W.

The Incompatibility of Calomel and Antipyrine. I. A New Mercury Compound of Antipyrine. CESARE PADERI (*Arch. farm. sperim. sci. aff.*, 1918, **26**, 359—380; from *Chem. Zentr.*, 1919, iii, 226—227).—Poisonous symptoms are observed particularly in children to whom these substances have been administered simultaneously or after a certain interval, but nothing is definitely known with regard to the mode of action. The author has therefore investigated the mutual behaviour of these substances under various conditions. Reaction does not occur in the presence of water or of acid media, such as gastric juice. In the presence of alkalis, however, changes occur which cause a marked toxicity; the product is not mercuric chloride, but a metallo-organic compound, the composition of which depends on the relative quantities of alkali and calomel. If sufficient of the former is present to combine with the whole of the chlorine, the compound,

$$Hg[NMe(OH):C_{10}H_9ON]_2,$$

obtained by Astre and Ville by the action of mercuric oxide on antipyrine, is obtained; otherwise, a *substance* is produced which gives the reactions of antipyrine, but contains one atom of mercury and one of chlorine to each molecule of antipyrine, and to which the formula $HgCl\cdot NMe(OH):C_{10}H_9ON$ is ascribed. Metallic mercury is also formed.

The new substance forms needles grouped in rosettes, m. p. 92°, and is sparingly soluble in cold water. It is more poisonous than

mercuric chloride. It gives precipitates with hydrogen sulphide or ammonium sulphide, and deposits mercury on copper; it does not react with sodium carbonate or potassium hydroxide, and only gives a slight precipitate with ammonia. With potassium ferrocyanide, it gives a flaky precipitate soluble in excess to a solution which slowly turns blue on exposure to air. Potassium iodide gives a turbid solution, from which a white precipitate, soluble in the warm or in excess of the reagent, slowly separates. A white precipitate is formed with stannous chloride, which disappears on shaking. Gold chloride gives a yellow precipitate, which is reduced when warmed. The substance also shows the antipyrine reactions with ferric chloride and with nitrous acid. H. W.

Reaction of the Potassium Salts of 2-Thiol-5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole and 2 : 5-Dithiol-1 : 3 : 4-thiodiazole with Halogenated Organic Compounds. (SIR) PRAFULLA CHANDRA RÂY, PRAFULLA CHANDRA GUHA, and RADHA KISHEN DAS (T., 1919, **115**, 1308—1312).

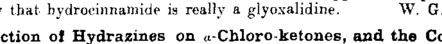
Photochemical Transformations in the Triphenylmethane Series. I. LIFSCHITZ [with CH. L. JOFFÉ] (*Ber.*, 1919, **52**, [*B*], 1919—1926).—When triphenylmethane dyes are mixed with potassium cyanide, they change into colourless triarylacetonitriles (Hantzsch, *A.*, 1900, i, 256; Müller, *A.*, 1910, i, 868). It is now shown that these colourless nitriles are rearranged into the coloured triphenylmethane cyanides when exposed to the light of an iron arc in methyl- or ethyl-alcoholic solutions in quartz vessels, as, for example, in the *p*-rosaniline series, $(NH_2\cdot C_6H_4)_3C\cdot CN \longrightarrow [(NH_2\cdot C_6H_4)_3{:}C]CN$. Solvents like benzene, ether, and chloroform have no effect, because of their small dissociating power, but solutions in dilute mineral acids also remain colourless (provided that the nitrile is pure), the explanation in this case being that the selective absorption of the necessary long-wave ultra-violet light is prevented by the participation of the amino-groups in salt formation. Further evidence of the production of the ionisable salts is the fact that the electrical conductivity of the alcoholic solutions increases on exposing them to the light. The experimental evidence (absorption curves, etc.) is based on the cases of pararosaniline and crystal-violet. J. C. W.

Oxidation of the Hydramides. J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1919, **169**, 978—980).—The three hydramides examined, benzhydramide, anishydramide, and piperonhydramide, on oxidation with iodine and sodium carbonate, all gave a 30—40% yield of the corresponding cyanidine. These cyanidines were subjected to hydrolysis with hydrochloric acid in acetic acid solution at a temperature not exceeding 120°. Under these conditions, triphenylcyanidine gave benzoic acid, ammonia, and benzamidine. Trimethoxyphenylcyanidine, $(OMe\cdot C_6H_4\cdot CN)_3$, and trimethylene-

dioxyphenylcyanidine, $(CH_2{:}O_2{:}C_6H_3{\cdot}CN)_3$, gave results of the same order.

Hydrocinnamide when oxidised by iodine and sodium carbonate did not give the corresponding cyanidine, but only an amorphous resin. The author considers that this result supports Delépine's view that hydrocinnamide is really a glyoxalidine. W. G.

Action of Hydrazines on α-Chloro-ketones, and the Constitution of the so-called Tetraphenyltetracarbazone. SVEN BODFORSS (*Ber.*, 1919, **52**, [*B*], 1762—1775).—In 1886, Hess obtained a yellow compound, m. p. 137°, by the action of phenylhydrazine on ω-bromoacetophenone in ice-cold alcohol, and assigned to it the formula $NPh<\begin{matrix}-N\\CH_2\end{matrix}>CPh$. This substance has been investigated by Culmann (A., 1890, 1268), who proposed a doubled formula, $C_{28}H_{24}N_4$, from very erroneous arguments, and the constitution of a tetraphenyltetracarbazone; Bender (A., 1888, 53, 1188); and Freer (A., 1899, 358); and recently Scholtz (A., 1918, i, 96), obtained a colourless compound, m. p. 174°, by condensing the agents in boiling alcohol, which he regarded as tetraphenyl-β-tetracarbazone (I), that is, as an isomeride of Hess's compound. From an analogy with the action of ammonia on ω-bromoacetophenone, which results in the formation of pyrazines (Tutin and Caton, T., 1910, **97**, 2495), it is more than likely that Scholtz's compound is 1:4-dianilino-2:5-diphenylpyrazine (II) or the -2:6-isomeride.



(I.) (II.)

In order, in the first place, to get a correct idea of the molecular formula for Hess's compound, the author condensed ω-*p*-dichloroacetophenone with phenylhydrazine under the same conditions, and obtained a product of the empirical formula $C_{14}H_{11}N_2Cl$. This confirms $C_{14}H_{12}N_2$ as the simplest formula for Hess's compound, and as the molecular weight in boiling benzene is a little more than 200, this is also the molecular formula. Various alternative structural formulæ are critically examined, and arguments are advanced in favour of Hess's original suggestion. The substance should therefore be designated 1:3-*diphenyl*-Δ^2-1:2-*diazene*.

The product given by phenylhydrazine and ω-*p*-dichloroacetophenone is, consequently, 1-*phenyl*-3-p-*chlorophenyl*-Δ^2-1:2-*diazene*, $NPh<\begin{matrix}-N\\CH_2\end{matrix}>C{\cdot}C_6H_4Cl$; it crystallises in felted masses of thin, yellow needles, m. p. 164—164·5°. ω-Bromoacetophenone and *p*-bromophenylhydrazine yield 3-*phenyl*-1-p-*bromophenyl*-Δ^2-1:2-*diazene*, orange, glistening needles, m. p. 165° (decomp.), that is, a substance quite distinct from Freer's azo-compound, formed according to the scheme: $C_6H_5{\cdot}COMe + NH_2{\cdot}NH{\cdot}C_6H_4Br \longrightarrow$

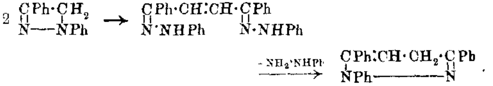
$$C_6H_4Br{\cdot}NH{\cdot}N{:}CPhMe \longrightarrow C_6H_4Br{\cdot}NH{\cdot}NH{\cdot}CPh{:}CH_2 \xrightarrow{\text{air}}$$

$C_6H_4Br·N:N·CPh:CH_2$, with which it should be identical if Freer's interpretation of Hess's reaction is correct; thus,

$C_6H_5·CO·CH_2Br + NH_2·NH·C_6H_4Br \longrightarrow$
$C_6H_4Br·NH·N:CPh·CH_2Br \longrightarrow C_6H_4Br·NH·NH·CPh:CHBr \xrightarrow{-HBr}$
$C_6H_4Br·N:N·CPh:CH_2$.

Phenylhydrazine and *p*-chloroacetylanisole yield *1-phenyl-3-p-anisyl-Δ^2-1:2-diazene*, yellow, felted needles, m. p. 141° (decomp.).

When Hess's compound is treated with acids (best, alcoholic hydrogen chloride in the cold), it yields a compound, $C_{22}H_{18}N_2$, which Culmann regarded as a phenylhydrazine derivative of diphenacyl, since he obtained diphenacyl from it on boiling with 30% sulphuric acid. Freer, however, considered it to be the phenylhydrazone of deoxybenzoin. It is now found that Culmann was correct, for the compound (white needles, m. p. 114°) may be prepared by condensing diphenacyl with phenylhydrazine. The formation of this *1:3:6-triphenyl-1:4-dihydropyridazine* from the diazene is explained in this way:



Phenylmethylhydrazine condenses with ω-bromoacetophenone to form the phenylmethylosazone of phenylglyoxal, orange needles, m. p. 152° (Culmann). The same product is obtained by heating phenylmethylhydrazine with phenacylanilide, but in another *modification*, thin, orange-red, shimmering leaflets, m. p. 153—154°.

The reaction between chloroacetone and phenylhydrazine at low temperatures was described by Bender. The product is purified by crystallisation from methyl alcohol, whereby the m. p. is raised from 158° to 162·5°, and its properties suggest that it is the *phenylhydrazone of phenylhydrazinoacetone*,

$NHPh·NH·CH_2·CMe:N·NHPh$.

For example, it is oxidised by nitrous acid to methylglyoxalosotetrazone (von Pechmann, A., 1888, 1288). J. C. W.

The Coupling of Diazo-compounds with Hydrocarbons. Kurt H. Meyer (*Ber.*, 1919, **52**, [*B*], 1468—1476).—In the majority of cases, the first step in the coupling of a compound with a diazonium salt is supposed by the author to be addition at double linkings (A., 1914, i, 882), but Karrer holds the opinion that addition at the amino-, hydroxy-, or alkyloxy-group represents the initial stage (A., 1915, i, 1073). It is now shown that certain unsaturated hydrocarbons can couple with suitable diazo-compounds, forming typical azo-derivatives, which indicates that, whilst Karrer's hypothesis may undoubtedly be correct in certain cases, addition at double bonds plays the principal rôle.

[With VIKTOR SCHOELLER.]—Butadiene couples with diazotised 2:4-dinitroaniline in glacial acetic acid to form *α-2:4-dinitrophenylazo-Δ^{αγ}-butadiene*, $CH_2:CH\cdot CH:CH\cdot N:N\cdot C_6H_3(NO_2)_2$, in brilliant yellow needles, m. p. 111° (decomp.). Piperylene couples with the nitrobenzenediazonium chloride to form *p-nitrophenylazopiperylene*, $C_{11}H_{11}O_2N_3$, glistening, yellow needles, m. p. 137°, and *2:4-dinitrophenylazopiperylene*, $C_{11}H_{10}O_4N_4$, orange-yellow crystals, which darken at 105° and have m. p. 131° (decomp.). Isoprene forms *2:4-dinitrophenylazoisoprene*,

$$C_{11}H_{10}O_4N_4,$$

orange-yellow crystals, m. p. 98° (decomp.). The best results are obtained with βγ-dimethyl-Δ^{αγ}-butadiene, and it is rather suggestive that a methyl group in the β-position should have this favourable influence, for *m*-cresol methyl ether couples more readily than anisole (Auwers and Michaelis, A., 1914, i, 744). *α-p-Nitrophenylazo-βγ-dimethyl-Δ^{αγ}-butadiene*,

$$CH_2:CMe\cdot CMe:CH\cdot N_2\cdot C_6H_4\cdot NO_2,$$

forms long, yellow needles, m. p. 177°, gives an *additive* compound with mercuric chloride, brilliant red needles, decomp. 109°, a dark violet compound with stannic chloride, and a *tetrabromide*, $C_{12}H_{13}O_2N_3Br_4$, dull orange, microscopic needles, m. p. 132° (decomp.), and may be reduced by means of tin and hydrochloric acid to *α-p-aminophenylhydrazo-βγ-dimethyl-Δ^{αγ}-butadiene*,

$$CH_2:CMe\cdot CMe:CH\cdot N_2H_2\cdot C_6H_4\cdot NH_2,$$

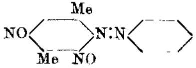
a pale greenish-yellow base, m. p. 125° (decomp.), which is very easily oxidised on exposure to air. *α-2:4-Dinitrophenylazo-βγ-dimethyl-Δ^{αγ}-butadiene* crystallises in bundles of slender prisms, decomp. 126°. J. C. W.

Aromatic Nitro-derivatives. VIII. Action of Phenylhydrazine on Trinitro-*p*-xylene and on Ethers of Trinitro-*m*-cresol. M. GIUA (*Gazzetta*, 1919, **49**, ii., 146—152. Compare A., 1918, i, 552).—Since trinitro-*p*-xylene contains a nitro-group which is readily replaceable, the action on it of phenylhydrazine should yield 3:5-dinitro-2-benzenehydrazo-*p*-xylene. Although formation of the latter in the first phase of the reaction may be assumed, it is found that the reaction proceeds further, reduction of a nitro-group and simultaneous elimination of a molecule of water from the ·NH·NH· group and another nitro-group in the ortho-position to it resulting in the formation of a 3:5-dinitroso-2-benzeneazo-*p*-xylene as final product; this is accompanied by 3-nitro-5-nitroso-2-benzenehydrazo-*p*-2-xylene, which represents an intermediate product.

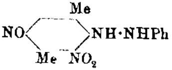
The methyl and ethyl ethers of trinitro-*m*-cresol react in the same way as trinitroanisole (compare Giua and Cherchi, succeeding abstract) with phenylhydrazine, the alkyloxy-group being replaced by the phenylhydrazine residue, with formation of 3-benzenehydrazotrinitrotoluene. The latter is, however, so unstable that when heated to boiling with alcohol it is transformed immediately into 3-benzeneazonitrodinitrosotoluene; during this change, the alcohol is converted into aldehyde, the second nitro-

group in the ortho-position to the hydrazo-group being reduced and a molecule of water simultaneously eliminated from the hydrazo-group and the other nitro-group.

3:5-*Dinitroso-2-benzeneazo*-p-*xylene* (I) forms shining, yellow



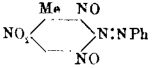
(I.)



(II.)

plates, m. p. 185°, and yields a dark coloration when heated with potassium hydroxide in alcoholic solution.

3-*Nitro-5-nitroso-2-benzenehydrazo*-p-*xylene* (II) forms shining, red, prismatic plates melting at 145° to a red oil, which readily decomposes if the heating is prolonged. With alkali and alcohol in the hot, it gives a deep red coloration, and when heated in presence of alcohol it is converted into the preceding compound.

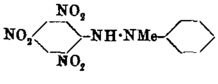


6-*Nitro-2 : 4-dinitroso-3-benzeneazotoluene* (annexed formula) forms pale yellow, silky needles, m. p. 148—149°. Under the influence of light it becomes brownish-yellow, and with alkali in alcoholic solution it produces a reddish-brown coloration.

T. H. P.

Aromatic Nitro-compounds. IX. Behaviour of Trinitroanisole. M. GIUA and F. CHERCHI (*Gazzetta*, 1919, **49**, ii, 152—157).—According to Masland and Sparre (A., 1913, i, 853), trinitroanisole is hydrolysed, even in the cold, by solutions of alkali carbonates, with formation of picrates, and to some extent by water in the hot, with formation of methyl alcohol and picric acid, whilst cold water exerts only slight hydrolysing action. The authors regard this so-called hydrolysis as a process of substitution in the methoxy-group; this group is easily replaceable, even by radicles of organic bases, in consequence of the ortho-para-influence of the nitro-groups present in the molecule.

Trinitroanisole may be used with advantage to replace picryl chloride in many organic syntheses. Thus, with hydrazine hydrate it gives 2:4:6-trinitrophenylhydrazine; with phenylhydrazine, either trinitrohydrazobenzene or nitrodinitrosoazobenzene, according to the temperature, and with aniline, trinitrodiphenylamine, from which hexanitrodiphenylamine may be obtained by further nitration. The conditions necessary for all these reactions have been determined.



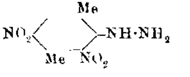
The action of *as*-phenylmethylhydrazine on trinitroanisole yields 2 : 4 : 6-*trinitro*-N′-*methylhydrazobenzene* (annexed formula), which crystallises in reddish-yellow or intense garnet-red prisms (probably

isomeric), m. p. 153°, and dissolves in concentrated sulphuric acid with a dark red coloration, and in alkali with a dark green coloration.

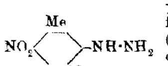
T. H. P.

Aromatic Nitro-derivatives. XI. Action of Hydrazine Hydrate on Aromatic Nitro compounds. M. GIUA (*Gazzetta*, 1919, **49**, ii, 166—175).—The action of hydrazine hydrate on various aromatic nitro-derivatives containing a labile nitro-group has been investigated. With trinitro-*p*-xylene and *β*- and *γ*-trinitrotoluenes, the reaction occurs readily in alcoholic solution, the labile nitro-group being replaced by the hydrazine residue. With the methyl ether of trinitro-*m*-cresol under the same conditions, the ortho-para-influence exerted by the nitro-groups on the methoxy-group brings about replacement of the latter by the hydrazine residue.

3 : 5-*Dinitro*-p-2-*xylylhydrazine* (annexed formula), prepared from trinitro-*p*-xylene and hydrazine hydrate, forms yellow prisms, m. p. 180° (decomp.), and with alkalis, in either alcoholic or acetone solution, gives a brick-red coloration. Its *β-acetyl* derivative, $C_6HMe_2(NO_2)_2$·NH·NHAc, forms pale yellow, shining plates, m. p. 232° (decomp.), and gives a dark red coloration with alkalis in alcoholic solution. The *β-benzylidene* derivative, $C_6HMe_2(NO_2)_2$·NH·N:CHPh, forms long, pale yellow needles, m. p. 221° (decomp.), and dissolves in potassium hydroxide to an intense violet-red solution. The *β-anisylidene* derivative, $C_{16}H_{16}O_5N_4$, crystallises in slender, golden-yellow needles, m. p. 224° (decomp.), and yields an intense carmine-red coloration with potassium hydroxide.

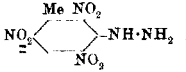


4 : 6-*Dinitro*-m-*tolylhydrazine* (annexed formula), prepared from *γ*-trinitrotoluene and hydrazine hydrate, forms reddish-yellow crystals, m. p. 194° (decomp.), its alcoholic solution being coloured intensely red by addition of an alkali.



The action of hydrazine hydrate on *β*-trinitrotoluene in alcoholic solution yields a *compound* which contains 28·31—28·7% N, and crystallises in golden-yellow prisms, m. p. 150° (decomp.); it may possibly be an aziminole derivative of the formula $NO_2·C_6H_2Me<\genfrac{}{}{0pt}{}{N}{N(OH)}>N$.

2 : 4 : 6-*Trinitro*-m-*tolylhydrazine* (annexed formula), prepared by the action of hydrazine hydrate on the methyl ether of trinitro-*m*-cresol (m. p. 94°; Larter, P., 1901, 183, gave m. p. 91°) (compare this vol., i, 19), crystallises in shining, golden-yellow plates, m. p. 176° (gas evolution), and dissolves in alkali solution, giving a brownish-red coloration. The *β-acetyl*



derivative, $C_9H_9O_7N_5$, forms large, yellow prisms, m. p. 136°, and gives a red coloration with alkali in alcoholic solution. The *αβ-diacetyl* derivative, $C_6HMe(NO_2)_3{\cdot}NAc{\cdot}NHAc$, crystallises in nacreous plates, m. p. 216° (decomp.), and gives a dark red coloration with alkali in alcoholic solution. The *benzylidene* derivative, $C_{14}H_{11}O_6N_5$, forms small, reddish-yellow prisms, m. p. 249—250° (decomp.), burns with difficulty, leaving considerable carbonaceous residue, and dissolves in alkali solutions, giving an intense brick-red coloration. T. H. P.

The Proteolytic Activity of Pancreatic Amylase Preparations. H. C. Sherman and Dora E. Neun (*J. Amer. Chem. Soc.*, 1919, **41**, 1855—1862).—The experiments were undertaken with a view to throwing some further light on the nature of the relationship which exists between the amylolytic and proteolytic activities of purified pancreatic amylase preparations. High-grade commercial pancreatin was purified as described previously (Sherman and Schlesinger, A., 1912, i, 815; 1915, i, 604; Sherman and Neun, A., 1918, i, 414), except that in the final precipitation the usual 1:1 alcohol–ether mixture was replaced by a 2:1 mixture. A precipitate (*A*) is thus obtained, after removal of which a second precipitate (*B*) is isolated by adding more ether to the filtrate. The amylolytic activity of *A* is found to be lower than that of *B*, but the latter was more active than the usual amylase preparations; the proteolytic activity was higher in precipitate *A* than in precipitate *B*. Interpretation of the results is rendered difficult by the exceedingly unstable nature of the material under purification and the impossibility of pushing the fractionation further, because of the great tendency to loss of amylolytic activity when pancreatic amylase in the absence of salts and carbohydrates is held in solution or subjected to precipitation. On the whole, it seems probable that a partial separation of a mixture of amylase and protease was accomplished, but that amylolytic activity was partly lost because of the extra manipulation, since amylolytic activity deteriorates much more rapidly than proteolytic, at least under conditions such as obtained in these experiments. The further possibility that there are enzyme particles which have both amylolytic and proteolytic activities is not excluded. H. W.

Influence of Aspartic Acid and Asparagine on the Enzymic Hydrolysis of Starch. H. C. Sherman and Florence Walker (*J. Amer. Chem. Soc.*, 1919, **41**, 1866—1873. Compare Sherman, Walker, and Caldwell, A., 1919, i, 559).—The action of saliva, pancreatin, and purified pancreatic amylase on alkali-washed potato, wheat, m[...] Lintner" soluble starch, is acceler[...] [...]nounts of boiled, neutralised wate[...] [...]e action of the vegetable amylas[...] [...]the addition of potato extract.

The addition of [...] [...]ragine accelerated

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the action of saliva, pancreatin, and purified pancreatic and malt amylases. Clear evidence of activation was not obtained in the case of malt extract or of the preparations made from *Aspergillus oryzae*.

The addition of both sodium aspartate and asparagine to the same digestion mixture produces practically the same activation as does one of these substances alone. Thus the activating effects of the substances are interchangeable rather than additive. Activation is not due in these experiments to change in hydrogen-ion concentration or merely to a more favourable concentration of electrolyte. The amino-compounds to be tested were added to a substrate which already contained the optimum concentrations of sodium chloride and phosphate, the reported activation being thus additional to the activity induced by chloride and phosphate. Moreover, sodium aspartate is not interchangeable with sodium chloride in the activation of purified pancreatic amylase. The effects of other amino-acids are being studied similarly. H. W.

The Separation of Potato Tyrosinase into Components. Hugo Haehn (*Ber.*, 1919, **52**, [*B*], 2029—2041).—Potato tyrosinase can be separated by filtration into a thermolabile residue (α-tyrosinase) and a filtrate (activator), which is stable towards heat; when separately tested, neither component shows the tyrosine reaction, but the mixture of the two is again active. The inactive residue can be activated by the addition of the solution obtained hy boiling expressed potato juice in dilute acetic acid solution, and subsequent filtration, as also by the addition of an aqueous solution of the ash obtained by igniting the residne left on the evaporation of such a solution.

Toluene appears to act as an oxygen carrier; it is found that preservation of solutions beneath toluene does not inhibit the enzymic process of tyrosinase, as would be expected in consequence of the assumed exclusion of air. Further, it is shown that the alkaline solutions of pyrogallol become hrown even when preserved beneath a layer of toluene which is 8 cm. high. The result is not due to hydroclastic activity of toluene, since the pyrogallol solutions remain unchanged when the experiment is performed in an atmosphere of hydrogen. H. W.

Urease and the Radiation Theory of Enzyme Action. III. H. P. Barendrecht (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 29—45. Compare A., 1919, i, 604).—A continuation of previous work. From electrometric measurements of the hydrogen-ion concentration of phosphate solutions to which 8% of carbamide had been added, it is shown that the dissociation of water is decreased. The study of the urease action on carbamide was continued in solutions containing 5% of alcohol; all other conditions were the same as in the preceding experiments. It is shown that . is decreased from $10^{-13.78}$ to $10^{-13.98}$ by this addition, and the in astant *m* for the hydrolysis of carbamide is reduced from 0·00381

to 0·00335. The influence of enzyme concentration is also studied. The results indicate that above a definite concentration of urease the activity is constant, but below this value the activity decreases.
J. F. S.

Course of the Degradation of Urea by Urease. H. VON EULER and G. BRANDTING (*Biochem. Zeitsch.*, 1919, **97**, 113—123).—Urease preparations previously kept at 17·5°, 30°, 35°, 40°, 45°, and 50° respectively for some days have shown constant activity. The authors cannot therefore confirm the periodicity in the activity of urease observed by Groll (A., 1919, i, 425). Groll's results are *discussed*.
S. S. Z.

Biochemistry of the Enzyme of Soja Beans (Urease). D. H. WESTER (*Chem. Weekblad*, 1919, **16**, 1442—1454).—A continuation of the author's previous research (A., 1916, ii, 502). The *urease content of a solution, if not too dilute, may be estimated* from the amount of urea which has undergone conversion. Neither the concentration of the urea solution nor the conversion products obtained affect the action of the enzyme. Urease solution retains its activity after prolonged storage, but it is necessary, on the other hand, to use freshly made urea solutions. For extracting the urease from the soja beans, glycerol to the extent of 50% may be added to the solution with advantage, but increased amounts will reduce the proportion of urease, and, further, the addition of glycerol to the mixture of urease and urea retards the enzymic process. The author finds that in some respects extract of Canavalia beans acts similarly to that of soja beans, but this investigation is still incomplete.
W. J. W.

A Peculiarity of the Enzymic Action of Soja-bean Extract at 37°. D. H. WESTER (*Chem. Weekblad*, 1919, **16**, 1461—1463).—Heating the extract for three days at 37° was found to reduce its efficiency, but heating for longer periods did not reduce the enzymic action proportionately. The following results were obtained:

	Hours.	Days.				
Time	3	7	14	21	28	35
Urea equivalent	126	47	38·2	90	85	60·3

The curve representing the above results is therefore a zigzag.
W. J. W.

Action of Urease at 35°. J. TEMMINCK GROLL (*Chem. Weekblad*, 1919, **16**, 1527).—The author confirms Wester's investigations (preceding abstract). He states that this behaviour is not a characteristic of one particular preparation, but is an actual property of urease and probably also of other ferments, such as lipases and ptyalin.
W. J. W.

The Action of Neutral Salts on the Osmotic Pressure and other Qualities of Gelatin. JACQUES LOEB (*Proc. Soc. Biol. Med.*, 1918, **15**, 129—131).—According to the author's hypothesis, neutral salts act on proteins, which, like gelatin, are stronger acids than bases, by forming metal proteinates. The anion either does not enter into combination at all with the gelatin or enters into a combination where its influence on the protein is not felt. When gelatin has been previously treated with an acid, for example, hydrochloric acid, gelatin chloride or hydrochloride is formed, which dissociates into a positive gelatin ion and a negative chlorine ion. Neutral salts act on such gelatin chloride by exchanging their anion for the protein. This explains why the increase in the osmotic pressure and the viscosity, and the swelling of gelatin caused by the salt, do not become noticeable unless the excess of salt is washed away, since the presence of the salt represses the electrolytic dissociation of the gelatin salt formed.

CHEMICAL ABSTRACTS.

New Organic Compounds of Phosphorus. H. STAUDINGER and JULES MEYER (*Helv. Chim. Acta*, 1919, **2**, 612—618).—Previous attempts to obtain a compound in which a nitrogen atom is directly united to five carbon atoms having proved unsuccessful (this vol., i, 34), the authors have turned their attention to the preparation of a similar compound from phosphorus, since, in general, this element shows a greater tendency to pass into the quinquevalent condition than does nitrogen.

Attempts to prepare phosphorus pentaethyl from tetraethylphosphonium iodide and zinc ethyl did not give the desired result, since action did not occur at low temperatures, whilst at 150° the products were butane and an additive product of triethylphosphine and zinc iodide. Triethylphosphine did not react with zinc ethyl or with magnesium ethyl bromide, whilst a phosphinemethylene derivative could not be prepared from triethylphosphine oxide and diphenylketen. The latter, however, unites readily with triethylphosphine (but not with triphenylphosphine) in absolute ethereal solution, yielding the unstable, pale yellow, crystalline additive *product*, $Et_3P<\begin{matrix}O\\|\\C:CPh_2\end{matrix}$, which sinters at 80° and is completely decomposed at 100°. When heated, it dissociates into triethylphosphine and diphenylketen, and a similar phenomenon is observed when it is dissolved in benzene. It is decomposed by water into triethylphosphine and diphenylacetic acid.

Hofman has shown that triethylphosphine combines readily with carbon disulphide, and has formulated the product as a derivative of carbamide; since, however, it shows the closest analogy to the keten additive compound, the authors assign to it the structure $Et_3P<\begin{matrix}S\\|\\C:S\end{matrix}$, which has previously been suggested by Jacobson (*Lehrbuch org. Chemie*, i, 427). When gently heated, it dissociates into carbon disulphide and triethylphosphine, whilst at a higher

temperature it yields triethylphosphine sulphide (the simultaneous formation of carbon monosulphide could not be established). The additive compound of triethylphosphine and phenylthiocarbimide is dissociated by gentle heating.

Carbodiphenyldi-imide does not react with triethylphosphine.

H. W.

New Organic Compounds of Phosphorus. II. Phosphazines. H. STAUDINGER and JULES MEYER (*Helv. Chim. Acta*, 1919, **2**, 619—635).—Tertiary phosphines combine more or less readily with the most varied aliphatic diazo-compounds, yielding derivatives, for which the name phosphazines is proposed, in accordance with the scheme $CR_2{:}N{:}N + PR_3 \longrightarrow R_2C{:}N{-}N{:}PR_3$. They are decomposed by water into the hydrazone and phosphine oxide. When heated, they lose nitrogen, but the exact course of the reaction has only been followed in the case of triphenylphosphinebenzophenoneazine, when triphenylphosphinediphenylmethylene is produced (compare preceding abstract). They have more or less strongly marked basic properties and unite with two molecules of a monobasic acid to form salts, the constitution of which is not definitely established.

Triethylphosphinefluorenoneazine, $PEt_3{:}N{\cdot}N{:}C{<}{C_6H_4 \atop C_6H_4}$, golden-yellow, rather unstable crystals, m. p. 160°, is prepared by the action of diazofluorene on triethylphosphine in benzene solution in an atmosphere of nitrogen. With methyl iodide, it yields the *product*, $C_{19}H_{23}N_2P,CH_3I$, pale yellow powder, m. p. 109—113°. It dissolves in dilute sulphuric and hydrochloric acids, and is recovered unchanged when the acid is neutralised; with the concentrated acids, it yields deep orange solutions, which become colourless on dilution with water. The yellow, crystalline *hydrochloride* is described. When hydrolysed with aqueous alcohol, it yields fluorenonehydrazine and triethylphosphine oxide, whilst with moist chloroform it yields *bisdiphenylenetetrahydrotetrazine* (?), orange-coloured crystals, m. p. about 325°.

Triphenylphosphinefluorenoneazine forms comparatively stable, compact, yellow crystals, m. p. 209—210° (decomp.). It is much more feebly basic than the triethylphosphine derivative, and neither unites with methyl iodide nor dissolves in dilute aqueous acids. The *hydrochloride* is an unstable substance which slowly loses hydrogen chloride when preserved; it softens at about 193°, but has not a definite m. p. *Phenyldiethylphosphinefluorenoneazine* is readily obtained in stable, yellow crystals, m. p. 115°, which are hydrolysed to fluorenehydrazone and phenyldiethylphosphine oxide, and is feebly basic in character; the *hydrochloride*, pale yellow crystals, m. p. above 250° (indefinite), is described.

Diphenyldiazomethane reacts very readily with triethylphosphine, but the product, *triethylphosphinebenzophenoneazine*,

$$PEt_3{:}N{\cdot}N{:}CPh_2,$$

is so unstable that it could not be isolated in the pure state; its

formation is inferred from the fact that benzophenonehydrazine is obtained by the immediate treatment of the crude product with alcohol. When preserved, it readily yields *bisdiphenyltetrahydrotetrazine*, pale yellow, crystalline powder, m. p. 204·5—205·5°. *Phenyldiethylphosphinebenzophenoneazine*, $PEt_2Ph\!:\!N\!\cdot\!N\!:\!CPh_2$ forms pale yellow crystals, m. p. 113°, and is hydrolysed to benzophenonehydrazone and phenyldiethylphosphine oxide. It dissolves in aqueous acids. *Triphenylphosphinebenzophenoneazine*,

$$PPh_3\!:\!N\!\cdot\!N\!:\!CPh_2,$$

is an almost colourless, stable, crystalline powder, m. p. 173° (decomp.). It is slowly hydrolysed to benzophenonehydrazone and triphenylphosphine oxide. It is scarcely affected by dilute acids. The colourless *hydrochloride* is a crystalline powder, m. p. ca. 185° (decomp.).

Triethylphosphine and phenyldiethylphosphine react with ethyl diazoacetate, but crystalline products could not be isolated; triphenylphosphine, on the other hand, yields *ethyl triphenylphosphineglyoxylate-azine*, $PPh_3\!:\!N\!\cdot\!N\!:\!CH\!\cdot\!CO_2Et$, colourless crystals, m. p. 113—114°.

Benzoylphenyldiazomethane reacts readily with triethylphosphine and triphenylphosphine. Benzoyldiazoacetic ester also reacts with both phosphines, yielding azines, which will be described subsequently.

The tervalent phosphorus atom of phosphorus phenyl dichloride and of phosphorus trichloride appears unable to undergo these additive reactions. H. W.

New Organic Compounds of Phosphorus. III. Phosphinemethylene Derivatives and Phosphineimines. H. STAUDINGER and JULES MEYER (*Helv. Chim. Acta*, 1919, **2**, 635—646).—An account is given of the preparation and properties of two new classes of derivatives, namely, triphenylphosphinediphenylmethylene, obtained by loss of nitrogen from triphenylphosphinebenzophenoneazine, as indicated in the preceding abstract, and phosphineimine compounds, produced by addition of azides to phosphines and spontaneous decomposition of the phosphazides primarily formed: $NPh\!:\!N\!:\!N + PPh_3 \longrightarrow NPh\!:\!N\text{–}N\!:\!PPh_3 \longrightarrow NPh\!:\!PPh_3$.

Triphenylphosphinediphenylmethylene, $PPh_3\!:\!CPh_2$, m. p. 170—172°, is best prepared by heating the corresponding azine in small quantities at a time in a vacuum at 185—195°. It crystallises from benzene in red leaflets, which contain approximately one molecule of benzene, which is only eliminated with difficulty. It dissolves in warm dilute hydrochloric acid, forming a colourless solution, from which *triphenylbenzhydrylphosphonium chloride*, colourless needles, m. p. 240—242°, separates on cooling. When heated with a solution of sulphur in carbon disulphide, it forms thiobenzophenone and triphenylphosphine sulphide. It does not react with carbon disulphide, benzylideneaniline, dimethylaminobenzaldehyde, thiobenzophenone, or with diphenylketen. It

appears, therefore, to be considerably less reactive than diphenylketen, and its inability to unite with the latter is somewhat remarkable, more particularly since it is capable of reacting with phenylcarbimide to yield *diphenylketenphenylimine*.

Triphenylphosphinephenylimine, PPh_3:NPh, forms a pale yellow, crystalline powder or large plates, m. p. 131—132°, and is best prepared by the action of triphenylphosphine on phenylazide in absolute ethereal solution. It has feebly basic properties and dissolves to some extent in dilute sulphuric and hydrochloric acids; the boiling acids hydrolyse it to triphenylphosphine oxide and the aniline salt. It does not unite with substances containing a single double bond, such as benzaldehyde, benzylideneaniline, or thiobenzophenone. Reaction readily occurs, however, with compounds containing paired double linkings; thus, dry carbon dioxide at 130—140° converts it into triphenylphosphine oxide and phenylcarbimide, whilst triphenylphosphine sulphide and phenylthiocarbimide are formed with carbon disulphide. Triphenylphosphine oxide and triphenylphosphine sulphide are similarly obtained when it is gently warmed with phenylcarbimide and phenylthiocarbimide respectively. *Triphenylphosphine-p-tolylimine* forms pale yellow crystals, m. p. 134—135°, and is decomposed by carbon dioxide or carbon disulphide in the same manner as the phenylimine. *Triphenylphosphine-m-xylylimine* has m. p. 130—131°.

Phosphorus trichloride and phosphorus phenyl dichloride do not react with phenylazide.

Phenyldiethylphosphine and triethylphosphine in the undiluted condition react explosively with phenylazide. By conducting the action between the latter substances in the presence of absolute ether, it was found possible to isolate a crystalline *product*, golden-yellow leaflets, m. p. 68·5—69·5°, which was too unstable to permit further purification, but appears to have a nitrogen content higher even than that required for the phosphazide; triethylphosphine oxide was isolated from the ethereal mother liquor. H. W.

Aromatic Arsenic Compounds. I. Plan of Procedure for the Synthesis of Arsenicals for Chemotherapeutic Research. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1581—1587).—The general plan of a very comprehensive study of the chemotherapeutic value of arsenic compounds is developed. The authors consider that the salvarsan type of these substances has been fully investigated, and therefore turn their attention to products containing quinquevalent arsenic, using as starting point *p*-amino- or *p*-hydroxy-phenylarsinic acid or a similar derivative, and uniting this with an accessible group of simple type which is readily capable of chemical modification. They regard simplicity in chemical manipulation as a further essential to success. From these points of view, the following classes of compounds have been studied: diazoamino-compounds, A–N:N–NRR′ (in which A is the arylarsinic radicle and R and R′ hydrogen, alkyl, aryl, or substituted aryl groups),

azo-dyes, A–N:N–R (in which R is the aromatic coupler), *N*-substituted amides of *N*-phenylglycine-*p*-arsinic acid,

A–NH·CH_2·CO·NRR′

(in which R and R′ are hydrogen, alkyl, aryl, or substituted aryl groups), β-substituted carbamides of *N*-phenylglycine-*p*-arsinic acid, A·NH·CH_2·CO·NH·CO·NHR, substituted *N*-phenylglycyl derivatives of arsanilic acid, A–NH·CO·CH_2·NHR, substituted *o*-phenylglycine derivatives of arsanilic acid, A–NH·CO·CH_2·OR, and substituted amides of *o*-phenylglycollic acid and *p*-arsinic acid, A–*o*·CH_2·CO·NHR. Of these, the third type has up to the present yielded the most important results. H. W.

Aromatic Arsenic Compounds. II. The Amides and Alkyl Amides of *N*-Arylglycinearsinic Acids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1587—1600. Compare preceding abstract).—The condensation of sodium arsanilate with chloroacetic acid to yield phenylglycine-*p*-arsinic acid has been described previously (D.R.-P. 204664); the authors now find that reaction occurs readily between sodium *p*-aminophenylarsinate and the amide and alkyl amides of chloroacetic acid, yielding substances of the general formula

AsO_3H_2·C_6H_4·NH·CH_2·CO·NRR′,

in which R and R′ may be hydrogen, alkyl, benzyl, or substituted benzyl radicles. The best experimental conditions consist in boiling aqueous solutions of sodium arsanilate and the simpler chloroacetyl alkylamines for a half to two hours; in the case of the chloroacetylbenzylamines, 50% alcohol is the most serviceable medium, and the addition of sodium iodide is found to be necessary.

All the glycineamidearsinic acids are colourless, crystalline substances which are generally sparingly soluble in the usual neutral media and possess high melting or decomposition points, the latter depending greatly on the rate of heating. They dissolve in alkali hydroxides or carbonates to form neutral salts, from which they are entirely displaced by acetic acid. They are more feebly basic than arsanilic acid itself, their hydrochlorides being stable only in the presence of concentrated hydrochloric acid. On boiling with excess of alkali or with mineral acids, the amide linking is hydrolysed, with the formation of glycinearsinic acid and the amine.

The following individual substances are described: N(*phenyl*-p-*arsinic acid*)-*glycineamide* (N-*phenylglycineamide*-p-*arsinic acid*), aggregates of long, thin plates, which darken and soften without melting at 280° when rapidly heated (the *sodium* salt [+½H_2O] forms thin, nacreous plates readily soluble in water; the *potassium* and *ammonium* salts crystallise in thin, glistening, hexagonal, microscopic platelets; the *calcium* salt, microscopic, wedge-shaped prisms, is anhydrous; the *magnesium* salt forms a microcrystalline powder; heavy metal salts give immediate precipitates, the *silver* act withrming aggregates of thin, microscopic needles); N(*phenyl*-p-nzaldehyd*acid*)-*glycine methyl ester*, AsO_3H_2·C_6H_4·NH·CH_2·CO_2Me,

microscopic needles and thin plates, which soften and darken above 200° and decompose at about 285°; the corresponding *ethyl* ester, delicate needles, m. p. 270° (decomp.); N(*phenyl*-p-*arsinic acid*)-*nitrosoglycineamide*, $AsO_3H_2\cdot C_6H_4\cdot N(NO)\cdot CH_2\cdot CO\cdot NH_2$, silky needles, decomposing at 182—183°; N(*phenyl*-p-*arsinic acid*)-*glycinemethylamide*, microscopic plates, which darken and soften above 240° and decompose at 285°; N(*phenyl*-p-*arsinic acid*)-*glycine-ethylamide*, platelets, decomposing at 278—280° after darkening above 250°; N(*phenyl*-p-*arsinic acid*)-*glycine*-n-*propylamide*, microscopic needles, which do not melt below 280°; N(*phenyl*-p-*arsinic acid*)-*glycinedimethylamide*, microscopic needles, decomposing at about 241—242° when rapidly heated (the *sodium* salt, $+4H_2O$, is described); N(*phenyl*-p-*arsinic acid*)-*glycinediethylamide*, short needles, m. p. 199—201° (decomp.) after softening and darkening above 195°; N(*phenyl*-p-*arsinic acid*)-*glycinepiperidide*, microscopic needles, decomposing at 218—221° after softening and darkening above 200°; N(*phenyl*-p-*arsinic acid*)-*glycinebenzylamide*, microscopic needles, decomposing at 282—284°; N(*phenyl*-p-*arsinic acid*)-*glycine-3′-carboxylamidobenzylamide*,

$$AsO_3H_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot CO\cdot NH_2,$$

aggregates of microscopic needles, decomposing at 237—239° with preliminary darkening (the *sodium* salt, $+5H_2O$, is described); N(*phenyl*-p-*arsinic acid*)-*glycine*-4′-*acetylaminobenzylamide*, diamond-shaped plates, which do not melt below 280° (the *sodium* salt forms microscopic needles, $+4\cdot 5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine-3′-carboxylcarbamidobenzylamide*,

$$AsO_3H_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot CO\cdot NH\cdot CO\cdot NH_2,$$

delicate needles, decomposing at 239—240°; N(*phenyl*-p-*arsinic acid*)-*glycine-4′-carbamidobenzylamide*,

$$AsO_3H_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2;$$

N(*phenyl*-p-*arsinic acid*)-*glycine*-3′-*methyl*-4′-*acetylaminobenzylamide*, flat needles, decomposing at 278° (the *sodium* salt, $+6H_2O$, is described); N(*phenyl*-p-*arsinic acid*)-*a-aminopropionamide*, thin, hexagonal plates, darkening above 255° and decomposing at 262—263·5° (the *sodium* salt is described); *oxanilamide*-p-*arsinic acid*, $AsO_3H_2\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NH_2$, minute needles, which do not melt or decompose below 280°.

N(*Phenyl*-o-*arsinic acid*)-*glycineamide* crystallises in thin plates which decompose at 198—199°. N(*Phenyl*-m-*arsinic acid*)-*glycineamide* forms prismatic needles, m. p. 175—177° (decomp.), whilst the corresponding methylamide crystallises in flat, microscopic needles or platelets, m. p. 193—194·5° (decomp.).

The following derivatives of the aminotolylarsinic acids have been prepared: N(o-*tolyl*-4-*arsinic acid*)-*glycineamide*, delicate needles, which do not melt below 285°; N(o-*tolyl*-5-*arsinic acid*)-*glycineamide*, glistening platelets, decomposing at about 283° after darkening above 250°; N(m-*tolyl*-6-*arsinic acid*)-*glycineamide*, diamond-shaped platelets, m. p. 203—205° (decomp.); N-m-2-*xylyl*-5-*arsinic acid glycineamide*, plates or prisms, m. p. 236—237° (decomp.).

H. W.

Aromatic Arsenic Compounds. III. The Carbamides and β-Substituted Carbamides of N-Arylglycinearsinic Acids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1600—1610. Compare preceding abstracts). —By replacing the amides of chloroacetic acid by carbamide and its alkyl or aryl derivatives in the reaction described in the previous paper, the carbamides and substituted carbamides of the arylglycinearsinic acids,

$AsO_3H_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot NHR$

(where R may be hydrogen or an alkyl or aryl radicle), are obtained. The new series of substances closely resembles the amide series; they form stable and soluble neutral salts with the alkali metals. The carbamide linking, like that of the amides, is easily ruptured, this often occurring even at the ordinary temperature in solutions containing excess of alkali hydroxide. From the physiological point of view, the methylcarbamide of N-phenylglycine-p-arsinic acid is the most interesting member of the series. The following individual substances are described: *Derivatives of* p-*Arsanilic Acid.*—N(*Phenyl*-p-*arsinic acid*)-*glycinecarbamide*, microscopic needles, which darken, but do not melt, below 280° (the *sodium* salt [+2H₂O], hexagonal platelets, the *silver* salt, microscopic needles, and the *magnesium* salt are described); N(*phenyl*-p-*arsinic acid*)-*glycinemethylcarbamide*, long, thin, glistening needles, decomposing at 224—225° (the *sodium*, *silver* and *magnesium* salts were prepared); N(*phenyl*-p-*arsinic acid*)-*glycine-ethylcarbamide*, microscopic needles, decomposing at 223—225° (the *sodium* salt crystallises with $4 \cdot 5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycinebenzylcarbamide*, rosettes of needles, decomposing at 225°; α-N(*phenyl*-p-*arsinic acid*)-*aminopropionylcarbamide*, $AsO_3H_2 \cdot C_6H_4 \cdot NH \cdot CHMe \cdot CO \cdot NH \cdot CO \cdot NH_2$, minute needles which decompose at 225—226°; N(*phenyl*-p-*arsinic acid*)-*glycinephenylcarbamide*, long, fine needles, which darken and melt at 280° (the *sodium* salt, flat needles [$+5H_2O$], is described); N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*acetylaminophenylcarbamide*, flat, microscopic needles, decomposing at 265—266° after sintering and darkening above 240° (the *sodium* salt, flat needles [$+5H_2O$], was prepared); N(*phenyl*-p-*arsinic acid*)-*glycine*-m′-*oxamylaminophenylcarbamide*,

$AsO_3H_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot CO \cdot NH_2$,

microcrystalline powder, decomposing at 223—224°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*hydroxyphenylcarbamide*, microscopic needles ($+1 \cdot 5H_2O$), not melting in the anhydrous state below 280° (the *sodium* salt is described); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*carbamidophenoxyacetamide*,

$AsO_3H_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot NH \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CO \cdot NH_2$,

diamond-shaped platelets, decomposing at 243—244° after sintering and darkening (the *sodium* salt forms anhydrous plates); N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*carbamidobenzamide*, flat, microscopic needles, m. p. 213—214° (decomp.); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*carbamidobenzamide*, decomposing at 245° after

darkening above 230°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*carbamidophenylacetamide*, felted needles, which decompose at 214—216°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*carbamidophenylacetamide*, needles (+H_2O), decomposing when anhydrous at 218—221° (the *sodium* salt forms microscopic, hexagonal platelets).

Derivatives of o-*Arsanilic Acid*.—N(*Phenyl*-o-*arsinic acid*)-*glycinecarbamide*, delicate needles, m. p. 231—232° (decomp.) when rapidly heated; N(*phenyl*-o-*arsinic acid*)-*glycinemethylcarbamide*, minute needles, m. p. 218° (decomp.).

Derivatives of m-*Arsanilic Acid*.—N(*Phenyl*-m-*arsinic acid*)-*glycinecarbamide*, colourless, microscopic needles, decomposing at 208—209°; N(*phenyl*-m-*arsinic acid*)-*glycinemethylcarbamide*, m. p. 213—213·5° (decomp.).

Derivatives of Substituted Arsanilic Acids.—N(m-*Tolyl*-6-*arsinic acid*)-*glycinecarbamide*, delicate needles, decomposing at about 235° (the *sodium* salt forms glistening plates +$2H_2O$); N(m-*tolyl*-6-*arsinic acid*)-*glycinemethylcarbamide*, hair-like needles, decomposing at 218—219°; N(2-*hydroxyphenyl*-5-*arsinic acid*)-*glycinecarbamide*, flat, glistening needles (+1—1·5H_2O), decomposing when anhydrous at 203—205°. H. W.

Aromatic Arsenic Compounds. IV. Aromatic Amides of *N*-Arylglycinearsinic Acids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1610—1644. Compare preceding abstracts).—An extensive series of compounds has been prepared in accordance with the general scheme:

$$AsO_3HNa{\cdot}C_6H_4{\cdot}NH_2 + Cl{\cdot}CH_2{\cdot}CO{\cdot}NHAr \longrightarrow AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NHAr + NaCl.$$

In the cases of the more reactive chloroacetyl derivatives, reaction may be effected in boiling aqueous solution, but with the more stable compounds, 50% alcohol is a more suitable solvent, and sodium iodide should be added. In general, it is found that *m*-arsanilic acid condenses more readily than the ortho- or para-isomerides. The compounds have generally weakly basic and acidic functions; the free arsinic acids do not, as a rule, possess sharp melting or decomposition points, the values obtained depending greatly on the rate of heating. They are, on the whole, but sparingly soluble in the usual media. The sodium salts, on the other hand, dissolve more or less readily in water, and were prepared for convenience in biological testing, and also as a convenient means of purification of the compounds. The following individual substances are described.

Derivatives of p-*Arsanilic Acid*.—N(*Phenyl*-p-*arsinic acid*)-*glycineanilide*, $AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NHPh$, minute, delicate needles, which do not melt below 285° (the *sodium* salt, glistening scales [+$4H_2O$], and the *nitroso*-compound, flat, colourless needles [+H_2O], decomposing at 190—192°, are described); N(*phenyl*-p-*arsinic acid*)-*glycine*-o′-*toluidide*, needles, which are not decomposed

below 275° (*sodium* salt, long, narrow platelets [$+2\cdot5H_2O$]) N(*phenyl*-p-*arsinic acid*)-*glycine*-m'-*toluidide*, long, thin plate decomposing at 285°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p'-*toluidide* woolly masses of minute needles, which do not decompose below 280° (*sodium* salt, thin, curved, glistening needles $+3H_2O$) N(*phenyl*-p-*arsinic acid*)-*glycine*-α-*naphthylamide*, microscopic needles, which darken, but do not melt, below 280°; N(*phenyl*-p-*arsinic acid*)-*glycine*-β-*naphthylamide*, microscopic needles, decomposing at 285—286° to a red liquid (*sodium* salt, flat needles $+4\cdot5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycinediphenylamide*, long thin, microscopic leaflets ($+H_2O$), decomposing when anhydrous at 271—272°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p'-*chloroanilide* toothed, microscopic leaflets, which do not melt below 280°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p'-*iodoanilide*, broad, minute needles, which do not melt below 275° (*sodium* salt, needles $+3\cdot5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine*-p'-*nitroanilide*, thin, faintly yellow needles, not melting below 285°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p'-*acetylaminoanilide*, microscopic needles, which do not melt below 285° (*sodium* salt, minute, lustrous platelets); N(*phenyl*-p-*arsinic acid*)-*glycine*-p'-*aminoanilide* (by hydrolysis of the acetyl derivative or reduction of the corresponding nitro-compound), colourless, microscopic needles or platelets, decomposing at 253—254°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p'-*carbamidoanilide*, pale brown, microcrystalline aggregates ($+0\cdot5H_2O$), decomposing when anhydrous at 230° after darkening above 200° (*sodium* salt, microscopic needles $+4H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine*-4'-*methyl*-5'-*carbamidoanilide*, microscopic platelets and hairs, decomposing at 257—258° (*sodium* salt, crystalline powder $+3\cdot5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine*-m'-*oxamylaminoanilide*,

$$AsO_3H_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NH_2,$$

microcrystalline aggregates, which darken and partly decompose, but do not melt below 280°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-o'-*aminophenol*, lustrous crystals, m. p. 190° (decomp.) after preliminary darkening; N(*phenyl*-p-*arsinic acid*)-*glycine*-m'-*hydroxyanilide*, which is of special importance, owing to its reduction to arsenophenylglycinebis *m'*-hydroxyanilide; N(*phenyl*-p-*arsinic acid*)-*glycine*-4-*hydroxy*-o-*toluidide*, pink plates or prisms, decomposing at about 220—225°; N(*phenyl*-p-*arsinic acid*)-*glycine*-2'-*hydroxy*-p-*toluidide*, prisms, m. p. 258° (decomp.); N(*phenyl*-p-*arsinic acid*)-*glycine*-p'-*hydroxyanilide*, glistening platelets, m. p. 255—260° (decomp.) (*sodium* salt, lustrous leaflets $+4\cdot5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine*-p'-*anisidide*, lustrous leaflets, which darken and soften above 230°; N(*phenyl*-p-*arsinic acid*)-*glycine*-1-*hydroxy*-β-*naphthalide*, microscopic plates and prisms ($+2H_2O$), decomposing, when anhydrous at 189—191°; N(*phenyl*-p-*arsinic acid*)-*glycine*-4-*hydroxy*-α-*naphthalide*, microscopic crystals, decomposing, when anhydrous, at 240—242° after darkening above 200° (*sodium* salt, glistening plates $+5\cdot5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-4:6-*dichloro*-3-*hydroxyanilide*, flat, colourless, microscopic needles, m. p. about 280° (decomp.) after darkening above 200°; N(*phenyl*-p-*arsinic*

acid)-glycyl-6-bromo-3-hydroxyanilide, glistening leaflets, decomposing at 255°; N(*phenyl*-p-*arsinic acid*)-*glycine-3′:4′-dihydroxyanilide*, glistening leaflets, decomposing at about 260—265° after blackening above 200°; N(*phenyl*-p-*arsinic acid*)-*glycylanthranilic acid*, octahedra, which decompose at 230—235° (the corresponding *ethyl* ester forms needles which do not decompose below 280°); N(*phenyl*-p-*arsinic acid*)-*glycyl*-N-*methylanthranilic acid*, microscopic aggregates of needles or plates, decomposing at 230°; N(*phenyl*-p-*arsinic acid*)-*glycyl-2′-aminobenzamide*, microscopic needles ($+H_2O$), m. p. 170° (*sodium* salt, minute crystals $+4·5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*aminobenzamide*, irregular, microscopic platelets, which are not completely decomposed below 280°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*aminobenzoylcarbamide*, microscopic needles, decomposing at about 280° (*sodium* salt, microscopic hairs $+8H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminobenzamide*, microscopic needles, which do not melt below 280° (*sodium* salt, thin, microscopic needles $+4·5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl-5′-aminosalicylamide*, glistening scales ($+H_2O$), which, when anhydrous, softens above 190° and gradually decomposes until fluid at about 255°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*aminophenylacetamide*, microscopic needles, decomposing at 275—280° after darkening above 220°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenylacetic acid*, microscopic globules, m. p. 280° (decomp.); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenylacetamide*, microscopic hairs, which do not decompose below 280° (*sodium* salt, glistening platelets $+4·5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenylacetylcarbamide*, minute hairs, which do not melt below 280° (*sodium* salt, minute, hexagonal plates $+3H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-o′-*aminophenoxyacetamide*, minute needles, decomposing at about 280° with preliminary darkening; N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*aminophenoxyacetic acid*, decomposing at about 250—260° after softening at 180—190°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenoxyacetic acid*, flat, microscopic needles or platelets, which do not melt below 285° (*sodium* salt, glistening leaflets $+3H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenoxyacetamide*, flat needles which do not melt below 280° (*sodium* salt, microscopic needles $+5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenoxyacetylcarbamide*, microscopic needles, slowly decomposing at 290° (*sodium* salt, microscopic needles $+4H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl-3-methyl-4-aminophenoxyacetic acid*, microscopic needles, decomposing at 270° (*sodium* salt, well-defined needles); N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*aminobenzenesulphonamide*, flat, glistening needles, which decompose at about 265° with preliminary darkening; N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminobenzenesulphonic acid*, flat needles ($+2H_2O$), slowly decomposing when anhydrous, at 245—246°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminobenzenesulphonamide*, thin, microscopic leaflets and needles, which do not melt below 280°; N(*phenyl*-p-*arsinic acid*)-*glycyl-4-amino-6-hydroxybenzenesulphonic acid*, microscopic leaflets ($+1·5H_2O$), which, when anhydrous, softens and darkens above

200°, but does not melt below 275°; N(*phenyl*-p-*arsinic acid*)-*glycyl-4-aminoacetophenone*, long, fine hairs, which do not melt below 280°.

Derivatives of o-*Arsanilic Acid*.—N(*Phenyl*-o-*arsinic acid*)-*glycineanilide*, minute prisms ($+1H_2O$), melting with decomposition at 160—163° when anhydrous; N(*phenyl*-o-*arsinic acid*)-*glycine*-o'-*hydroxyanilide*, glistening needles ($+0.5H_2O$), m. p. (anhydrous) 151—153° (decomp.); N(*phenyl*-o-*arsinic acid*)-*glycine*-m'-*hydroxyanilide*, pink, microscopic platelets ($+2H_2O$), m. p. 103—105°, m. p. of anhydrous substance about 180° (decomp.) after softening at about 125—130°; N(*phenyl*-o-*arsinic acid*)-*glycine*-p'-*hydroxyanilide*, colourless, microscopic platelets, m. p. 208—209° (decomp.).

Derivatives of m-*Arsanilic Acid*.—N(*Phenyl*-m-*arsinic acid*)-*glycineanilide*, prisms, decomposing at 217—218°; N(*phenyl*-m-*arsinic acid*)-*glycine*-o'-*hydroxyanilide*, flat, microscopic needles, m. p. 190—192° (decomp.) (the *ammonium* salt forms minute needles); N(*phenyl*-m-*arsinic acid*)-*glycine*-m'-*hydroxyanilide*, minute, irregular platelets and flat needles ($+1.5H_2O$), decomposing, when anhydrous, at about 180—190°; N(*phenyl*-m-*arsinic acid*)-*glycine*-p'-*hydroxyanilide*, microscopic platelets, which slowly decompose at 180°.

Derivatives of Substituted and p-*Arsanilic Acids*.—N(o-*Tolyl*-5-*arsinic acid*)-*glycine*-m'-*hydroxyanilide*, long, flat, microscopic needles, which slowly darken and decompose at 285°; N(o-*tolyl*-5-*arsinic acid*)-*glycine*-p'-*hydroxyanilide*, spindle-shaped needles, decomposing at 232—233° with preliminary darkening; N(m-*tolyl*-6-*arsinic acid*)-*glycine*-m'-*hydroxyanilide*, spindle-shaped microcrystals, which decompose at 232—235° after softening and darkening; N(2-*carboxyphenyl*-4-*arsinic acid*)-*glycine*-m'-*hydroxyanilide*, minute platelets ($+1H_2O$), decomposing, when anhydrous, at 204—207° after darkening and swelling. H. W.

Aromatic Arsenic Compounds. V. *N*-Substituted Glycylarsanilic Acids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1809—1821. Compare preceding abstracts).—The substances under discussion are closely related to the previously described substituted anilides of phenylglycine-*p*-arsinic acid, but differ from these in the fact that the glycine side-chain is reversed, the arsinic radicle becoming a substituent on the anilide nucleus. The substances are readily prepared by boiling the sodium salt of chloroacetylarsanilic acid with the aromatic amino-compound in aqueous solution. The substituted phenylglycylarsanilic acids closely resemble the isomeric anilides of phenylglycine-*p*-arsinic acid, functioning both as acids and feeble bases. They are but sparingly soluble in the usual media, and all have high melting or decomposition points, the observed values depending on the rate of heating. In general, the sodium salts are readily soluble in water. The following individual substances have been prepared.

Chloroacetyl-*p*-arsanilic acid, $AsO_3H_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2Cl$ (compare D.R.-P. 191548), conveniently prepared by heating dry chloroacetic acid with *p*-arsanilic acid on the water-bath, minute, lenticular platelets and toothed leaflets, m. p. 285° (decomp.); *glycyl*-p-*arsanilic acid*, glistening plates, which do not melt below 295° (*iminobisacetyl*-p-*arsanilic acid*, micro-crystals, darkening without melting at 280—285°, is formed as by-product of the action of aqueous ammonia on chloroacetyl-*p*-arsanilic acid); N-*methylglycyl*-p-*arsanilic acid*, silky, glistening needles ($+2H_2O$), which darken at about 250°, but do not melt below 275°; N-*phenylglycyl*-p-*arsanilic acid*, felted needles, which do not melt below 280°; m-*oxaminophenylglycyl*-p-*arsanilic acid*,

$$CO_2H\cdot CO\cdot NH\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot AsO_3H_2,$$

decomposing, when anhydrous, at 179°, hydrated acid $+1H_2O$ (the *hydrochloride* is described); p-*aminophenylglycyl*-p-*arsanilic acid*, microcrystalline aggregates, which darken and soften, but do not melt, below 280°; p-*acetylaminophenylglycyl*-p-*arsanilic acid*, hexagonal platelets, not melting below 275° (the *sodium* salt forms flat, glistening needles $+7H_2O$); p-*oxaminophenylglycyl*-p-*arsanilic acid*, microscopic crystals $+1\cdot5H_2O$, darkening in the anhydrous state above 200°, but not melting below 275°; p-*oxamylaminophenylglycyl*-p-*arsanilic acid*, microscopic needles, not melting below 285° (the *sodium* salt was prepared); p-*carbamidophenylglycyl*-p-*arsanilic acid*, microscopic leaflets, which do not melt below 285°; m-*hydroxyphenylglycyl*-p-*arsanilic acid*, prisms $+3\cdot5H_2O$, which melt in their water of crystallisation at about 80° (the *hydrochloride* is described); p-*hydroxyphenylglycyl*-p-*arsanilic acid*, microscopic hairs ($+1H_2O$), which, when anhydrous, blacken and sinter above 200°, but do not melt entirely below 280° (the *sodium* salt, aggregates of microscopic needles $+H_2O$, was prepared); m-*carboxylamidophenylglycyl*-p-*arsanilic acid*, microscopic needles, decomposing at 248° (*sodium* salt, radiating masses of flat needles $+1H_2O$); N-*phenylglycineanilide*-m-*carboxycarbamide*-p′-*arsinic acid*,

$$AsO_3H_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO\cdot NH\cdot CO\cdot NH_2,$$

microscopic needles, decomposing at about 280° (*sodium* salt, flat, microscopic needles $+3H_2O$); p-*carboxylamidophenylglycyl*-p-*arsanilic acid*, microscopic prisms, which do not melt below 275° (*sodium* salt, glistening platelets $+2H_2O$); N-*phenylglycineanilide*-p-*acetamide*-p′-*arsinic acid*,

$$AsO_3H_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot CH_2\cdot CO\cdot NH_2,$$

microscopic platelets, decomposing at 256—258° after darkening and softening above 180°; N-*phenylglycineanilide*-p-*acetylcarbamide*-p′-*arsinic acid*, microscopic hairs $+0\cdot5H_2O$, which decompose, when anhydrous, at 270—273° after darkening above 230°; N-*phenylglycineanilide*-p-*oxyacetic*-p′-*arsinic acid*,

$$AsO_3H_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H,$$

minute, wedge-shaped plates $+1\cdot5H_2O$, decomposing in the anhydrous state at about 275° after darkening above 180°; N-*phenylglycineanilide*-p-*oxyacetamide*-p′-*arsinic acid*, woolly needles not melting below 265° (*sodium* salt, rosettes of flat, glistening needles $+4H_2O$); N-*phenylglycineanilide*-p-*oxyacetocarb*-

amide-p′-*arsinic acid*, minute platelets, which decompose at 257—258° with preliminary darkening (*sodium* salt, minute leaflets $+4H_2O$); N-*phenylglycineanilide*-p-*glycineamide*-p′-*arsinic acid*, micro-crystals ($+1.5H_2O$), which, when anhydrous, do not melt below 285°; N-*phenylglycineanilide*-4:4′-*diarsinic acid*,

$AsO_3H_2·C_6H_4·NH·CH_2·CO·NH·C_6H_4·AsO_3H_2$,

microscopic needles ($+0.5H_2O$), not melting below 280° when anhydrous; p-*acetylphenylglycyl*-p-*arsanilic acid*, microscopic needles, which darken and decompose when heated, but do not melt below 290° (*sodium* salt, pale yellow, glistening platelets $+3H_2O$).

H. W.

Aromatic Arsenic Compounds. VI. *N*-(Phenyl-*p*-arsinic acid)-*a*-phenylglycine and its Amides. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1822—1825. Compare preceding abstracts).—As a special extension of the general type of substances represented by the substituted amides, carbamides, and anilides of the phenylglycinearsinic acids, *N*(phenyl-*p*-arsinic acid)-a-phenylglycine,

$AsO_3H_2·C_6H_4·NH·CHPh·CO_2H$,

its amide, carbamide, and certain substituted anilides have been prepared. With the exception of the glycine itself, which was obtained by hydrolysis of the amide, the substances were made from sodium arsanilate and the phenylchloroacetylamino-compounds. It was found necessary to use sodium iodide and 50% alcoholic solution. The general properties of this group of substances are similar to those of the simpler glycine derivatives.

The following compounds are described: N(*phenyl*-p-*arsinic acid*)-a-*phenylglycine*, lustrous rhombic plates, decomposing at 202—203° after darkening and softening; N(*phenyl*-p-*arsinic acid*)-a-*phenylglycineamide*, microscopic needles, which do not melt below 280° (*sodium* salt, granular aggregates of plates $+3.5$ to $5H_2O$); N(*phenyl*-p-*arsinic acid*)-a-*phenylglycinecarbamide*, microscopic needles $+1H_2O$, decomposing when anhydrous at 195—197°; N(*phenyl*-p-*arsinic acid*)-a-*phenylglycine*-3′-*hydroxyanilide*, lenticular platelets $+1.5H_2O$, decomposing at 155—160°; the anhydrous substance has m. p. about 200—210° (decomp.), after softening at about 155—160°; N(*phenyl*-p-*arsinic acid*)-a-*phenylglycine*-4′-*carbamidoanilide*, decomposing at about 255° with preliminary darkening and softening; N(*phenyl*-p-*arsinic acid*)-a-*phenylglycine*-3′-*carbamidoanilide*, microcrystalline powder, m. p. 261—262° (decomp.); N(*phenyl*-p-*arsinic acid*)-a-*phenylglycyl*-4-*aminophenylacetamide*, $AsO_3H_2·C_6H_4·NH·CHPh·CO·NH·C_6H_4·CH_2·CO·NH_2$, minute plates and flat needles $+0.5H_2O$, melting in the anhydrous condition at 222—223° (decomp.).

H. W.

Aromatic Arsenic Compounds. VII. Substituted Benzyl-, Phenoxyethyl- and Phenacyl-arsanilic Acids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1826—1833. Compare preceding abstracts).—It has been

shown previously that the reactivity of the amino-group in arsanilic acid with chloroacetylamino-compounds is such as to render possible the synthesis of a very extensive series of aromatic arsinic acids. The authors now describe a preliminary series of experiments with other aromatic derivatives containing suitable alkyl haloid side-chains. Thus benzyl and substituted benzyl chlorides react with sodium arsanilate under suitable conditions to form benzyl- and substituted benzyl-arsanilic acids, reaction proceeding readily with negatively substituted benzyl chlorides. Similarly, the required derivatives are slowly formed from phenoxyethyl bromide and allied substances, whilst with phenacyl haloids the reaction also proceeds in the desired sense.

The following individuals are described: *benzyl*-p-*arsanilic acid*, arborescent masses of micro-crystals and larger prisms, decomposing at about 255° (*sodium* salt, glistening platelets); p-*nitrobenzylarsanilic acid*, yellow, microscopic needles, which do not melt below 280°; p-*aminobenzylarsanilic acid* (by reduction of the *p*-nitro-acid with ferrous hydroxide), microscopic leaflets, decomposing at about 202°; *3-nitro-4-hydroxybenzylarsanilic acid*, minute, yellow crystals ($+1H_2O$), decomposing when anhydrous at about 245—250° after darkening and sintering above 210° (*sodium* salt, thin, yellow, microscopic needles); *3-amino-4-hydroxybenzylarsanilic acid*, microscopic platelets ($+0{\cdot}5H_2O$), which do not melt below 285° when anhydrous; p-*carboxybenzylarsanilic acid*, microscopic needles which do not melt below 280° (*sodium* salt, microcrystalline powder $+0{\cdot}5H_2O$); p-*carboxylamidobenzylarsanilic acid*, microscopic needles, not melting below 280° (*sodium* salt, thin plates $+2{\cdot}5H_2O$).

Phenoxyethylarsanilic acid, $OPh{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2$, glistening scales ($+1H_2O$), which, when anhydrous, do not melt below 280° (*sodium* salt, flat, microscopic needles $+3{\cdot}5H_2O$); p-*acetylaminophenoxyethylarsanilic acid*, thin, narrow plates which do not melt below 275° (*sodium* salt, colourless, microscopic platelets $+3H_2O$); o-*carboxylamidophenoxyethylarsanilic acid*, broad, microscopic needles not melting below 280°; *phenacylarsanilic acid*, $COPh{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2$, faintly yellow aggregates of delicate, microscopic needles, which decompose at 185—187°; *2-hydroxy-5-acetylaminophenacylarsanilic acid*, microscopic platelets, decomposing at 228°. [*3-Acetylamino-6-hydroxyphenacyl bromide*, from acetophenetidide, bromoacetyl chloride, and aluminium chloride, forms a drab-coloured powder, m. p. 133—135° (slight decomp.).] H. W.

Aromatic Arsenic Compounds. VIII. The Amides of (*p*-Arsinic Acid)-phenoxyacetic Acid and the Isomeric Phenoxyacetylarsanilic Acids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1834—1840. Compare preceding abstracts).—Chloroacetylamino-compounds react with sodium *p*-hydroxyphenylarsinate (compare D.R.-P. 216270) to yield arsinic acids which crystallise readily when pure, have high decomposition points, are sparingly soluble in the usual media, and are more strongly acidic than the amides of phenylglycinearsinic acid. The success of the condensation depends on the addition of

an extra molecule of sodium hydroxide in order to form the sodium phenoxide, and this condition depresses the yield in the cases in which the haloid contains a labile halogen atom. Similarly, the sodium salt of chloroacetylarsanilic acid reacts with phenols to yield phenoxyacetyl or phenyl ether glycollylarsanilic acids, which are more strongly acidic than the glycylarsanilic acids. On reduction, both of these groups of substances yield arsenoxides and arseno-compounds which will be more fully described in a later communication.

The following substances have been prepared: *methyl* (p-*arsinic acid*)-*phenoxyacetate*, $AsO_3H_2·C_6H_4·O·CH_2·CO_2Me$, lustrous plates, which partly melt at about 192—195° (decomp.); (p-*arsinic acid*)-*phenoxyacetamide*, rhombic, microscopic prisms, which do not melt below 280° (*sodium* salt, glistening platelets); (p-*arsinic acid*)-*phenoxyacetanilide*, minute prisms and microscopic plates, which darken slightly above 250°, but do not melt below 280°; (p-*arsinic acid*)-*phenoxyaceto*-m-*hydroxyanilide*, sandy powder, m. p. 238—240° (decomp.) (*sodium* salt, lustrous, microscopic needles and long, thin platelets); (p-*arsinic acid*)-*phenoxyaceto*-p-*hydroxyanilide*, curved, colourless, microscopic crystals, decomposing at 238—240° (the *sodium* salt and (?) nitroso-compound were prepared); (p-*arsinic acid*)-*phenoxyacetyl-4-aminophenylcarbamide*, microscopic needles, which darken and soften at about 230—240°, but do not melt entirely up to 265°.

Phenoxyacetylarsanilic acid, $OPh·CH_2·CO·NH·C_6H_4·AsO_3H_2$, colourless crystals which darken slightly above 250°, but do not decompose below 280°; p-*oxaminophenoxyacetylarsanilic acid*, cream-coloured crystals, which darken but do not melt below 280° (a hydrated form $+1H_2O$ is also described); p-*carbamidophenoxyacetylarsanilic acid*, microscopic spindles, decomposing at about 280—283° with preliminary darkening (*sodium* salt, minute needles $+3H_2O$); o-*carboxylamidophenoxyacetylarsanilic acid*, delicate needles which do not decompose below 280° (*sodium* salt, prismatic needles $+5·5H_2O$); p-*carboxylamidophenoxyacetylarsanilic acid*, long, glistening needles, not melting below 280° (*sodium* salt, long, flat needles, $+7·5H_2O$). H. W.

Action of Arsenic Acid on Polyhydric Phenols. ADOLF SONN (*Ber.*, 1919, **52**, [*B*], 1704).—The polyhydric phenols suffer oxidation when heated with arsenic acid in the usual way, but if pyrogallol and dilute arsenic acid solutions are concentrated in a vacuum and left in the cold, a crystalline *pyrogallol arsenate*, $AsO[O·C_6H_3(OH)_2]_3$, is deposited. J. C. W.

1 : 3-Benzodiazolearsinic Acids and their Reduction Products. ROBERT REGINALD BAXTER and ROBERT GEORGE FARGHER (T., 1919, **115**, 1372—1380).

Organic Mercury Compounds Derived from p-Bromodi-Phenylaniline. FRANK C. WHITMORE (*J. Amer. Chem. Soc.*, JACOBS ... 1841—1854).—The paper is the first of a series in which **41**, 1826—...ction of mercury in the ortho-position to various substi-

tuted amino-groups will be studied. The reactions involved may be represented by the single equilibrium equation, $R_2Hg + HgX_2 \rightleftharpoons 2RHgX$, in which R represents any organic residue which has its free bond attached to carbon and X represents any univalent acid radicle. The reaction normally runs to completion to the right because of the slight solubility of the organo-mercuric salt, RHgX, in the organic solvents used. It may, however, be reversed by using reagents which remove HgX_2, such as alkaline reducing agents and compounds like potassium iodide and sodium thiosulphate, which form mercuric complexes of considerable stability.

5-Bromo-2-dimethylaminophenylmercuriacetate,

$$NMe_2\cdot C_6H_3Br\cdot HgC_2H_3O_2,$$

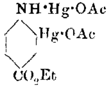
colourless needles, m. p. 144°, is prepared by the action of mercuric acetate on *p*-bromodimethylaniline in cool, aqueous alcoholic solution in 74% yield; simultaneously, smaller quantities of mercurous acetate and of a tar are produced. Formation of the latter is more pronounced in warm, concentrated solution; it can be suppressed to some extent by gradually adding the mercuric acetate to the well-agitated solution, but the yield of the mercury derivative also suffers. The mercury is not precipitated by hydrogen sulphide. The corresponding *chloride*, very fine needles, m. p. 183°, *bromide*, m. p. 182°, *iodide*, m. p. 169°, and *thiocyanate*, white, gritty crystals, m. p. 135°, decomposing at 140°, were obtained by the action of alcoholic solutions of the acetate on alcoholic solutions of calcium chloride, sodium bromide, potassium iodide, and potassium thiocyanate respectively. *5-Bromo-2-dimethylaminophenylmercurihydroxide*, from the acetate and sodium hydroxide in alcoholic solution, forms hard, nodular masses of crystals, m. p. 162°, and evolves gas without blackening at 165°. The *formate*, from the hydroxide and ethyl formate, crystallises in fine, felted needles, m. p. 145°, and decomposes at 150°.

Mercury di-5-bromo-2-dimethylaminophenyl, colourless needles, m. p. 123°, is most conveniently prepared (86% yield) by boiling a solution of the acetate in alcohol with potassium iodide, but the formation of *p*-bromodimethylaniline could not be suppressed completely. Reaction appears to depend on the formation of a stable iodine complex, M_2HgX_4, and evidence in support of this hypothesis is afforded by experiments with sodium or ammonium bromide or calcium chloride. The complexes formed by bromine and chlorine are less stable than those formed by iodine, and the yield of the mercury diphenyl compound drops to 3% with the bromides and to zero with the chloride. Conversion of the acetate into the mercury diphenyl derivative is less advantageously effected with sodium stannite solution (yield, 63%), and only very unsatisfactorily with sodium thiosulphate or potassium sulphide; with the latter reagent the *sulphide* was isolated as hard, white flakes which become grey at about 97° and partly melted at 115—120°. The formate, when heated for a protracted period in benzene alcoholic solution, yielded mainly mercury and *p*-bromodimethylaniline and a small quantity of the mercury diphenyl compound. Reduction of the acetate by

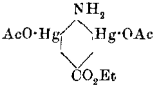
zinc dust in boiling alcoholic solution gave mercury, unchanged acetate, and *p*-bromodimethylaniline; with copper powder under similar conditions very little reaction occurred.

The mercury diphenyl derivative is quantitatively transformed into 5-bromo-2-dimethylaminophenylmercurichloride when heated with mercuric chloride in the presence of alcohol; the bromide, iodide, and thiocyanate may be obtained similarly and in good yield, but the iodide obtained in this manner is not nearly so pure as the corresponding bromide or chloride. When the mercury diphenyl derivative is heated in an analogous manner with mercuric sulphate, it yields basic mercuric sulphate and *p*-bromodimethylaniline. H. W.

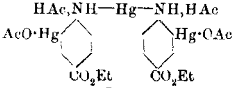
The Doctrine of Substitution. II. Mercuration of Ethyl *p*-Aminobenzoate. WALTER SCHOELLER, WALTER SCHRAUTH and ERWIN LIESE (*Ber.*, 1919, **52**, [*B*], 1777—1787. Compare A., 1914, i, 892).—When ethyl *p*-aminobenzoate is left with mercuric acetate in cold methyl alcohol, a pale yellow precipitate of *ethyl* N : 3-*diacetoxydimercuri-4-aminobenzoate* (I), m. p. 245°, is slowly deposited.



(I)

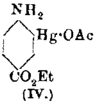


(II.)



(III.)

This is converted into *ethyl* 3 : 5-*diacetoxydimercuri-4-aminobenzoate* (II), a felted mass of long needles, m. p. 255—257°, on warming with glacial acetic acid, this being formed directly if acetic acid is used as the solvent in the first condensation. In a mixture of methyl alcohol and acetic acid, however, the white, microcrystalline *substance* (III), m. p. 230—240°, is produced. This is resolved into compound (I) and *ethyl 3-acetoxymercuri-4-aminobenzoate* (IV) (bundles of white needles, m. p. 182°, and again at 228°) on boiling with methyl alcohol, and into compounds (II) and (IV) on warming with glacial acetic acid. Compound (IV) is best obtained by melting the original agents together, when at 160° the mass solidifies again



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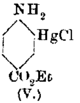

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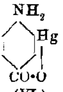


(VI.)

and the desired product may be extracted by hot methyl alcohol. Compounds (I) and (IV) react with sodium chloride in a mixture of methyl alcohol and acetic acid to form *ethyl 3-chloromercuri-4-aminobenzoate* (V), which crystallises in small, white prisms, m. p. 223°, but compound (II) differs from compound (I) in forming *ethyl 3:5-dichlorodimercuri-4-aminobenzoate*, small needles, m. p. 270°, under these conditions. When boiled with dilute sodium hydroxide, compound (IV) loses the ester and acetyl groups, and the sodium salt so formed deposits flocculent, white *3-hydroxymercuri-4-aminobenzoic anhydride* (VI) on acidification.

As a proof that the amino-group is free in compound (II), which is a type not produced in the case of anthranilic acid, the formation of its *acetyl* derivative (small needles, m. p. 247°) is advanced.

J. C. W.

Physiological Chemistry.

The Absence of the Bromine Reaction for Tryptophan in Tryptically Digested Leucocytes. MORITZ WEISS (*Bio-chem. Zeitsch.*, 1919, **98**, 116—120).—Tryptically digested leucocytes do not give the bromine reaction for tryptophan. Putrified pus shows the presence of indole, but only traces of indole derivatives can be demonstrated in it by the urorosein reaction (hydrochloric acid and sodium nitrite). The pus cells give a strong Adamkiewicz-Liebermann reaction. Whilst casein manifests a blue coloration, leucocytes give a violet coloration in this reaction. It is concluded that a derivative of tryptophan, but not tryptophan itself, is concerned in the synthesis of leucocytes. S. S. Z.

Origin of Odour. H. TEUDT (*Deutsch. Essigind.*, 1919, **23**, 160—162; from *Chem. Zentr.*, 1919, iii, 239).—The author has been able to develop his theory further by a consideration of the atomic models of Rutherford and Bohr, and has deduced the causes which are operative in setting the valency electrons within the molecule into such vibrations as produce odour (compare A., 1919, i, 607). The original paper must be consulted for details. H. W.

The Chromium Reaction of Certain Tissues as an Adrenaline Reaction. W. STOELTZNER (*Münch. med. Woch.*, 1919, **66**, 584; from *Chem. Zentr.*, 1919, iii, 60).—It has not been observed previously that adrenaline gives the same reaction with chromic acid as certain tissues. A dilute, pale yellow solution of potassium dichromate becomes intensely brown after addition of adrenaline, and gradually deposits a brown precipitate. The shade exactly matches the brown coloration assumed by the tissue when treated with dichromate, and the chromium reaction of the tissue must therefore be due to adrenaline. H. W.

Presence of Hæmatoporphyrin in the Urine and Fæces of a Case of Acute Hæmatoporphyrinuria. WILHELM LÖFFLER (*Biochem. Zeitsch.*, 1919, **98**, 105—116).—The coloured urine of a patient suffering from Landry's disease was examined for hæmatoporphyrin. The urine was precipitated with glacial acetic acid and the precipitate dissolved in potassium hydroxide. After reprecipitating and redissolving in $N/10$-potassium hydroxide, the fraction showed the typical spectrum of hæmatoporphyrin. A portion of the hæmatoporphyrin was methylated by H. Fischer's method. The compound thus obtained melted at 262° (not sharp), and gave the same spectrum as Fischer's preparation. The hydrolysed methyl ester yielded the original hæmatoporphyrin.

0·2 Gram of hæmatoporphyrin was excreted in twenty-four hours. On extracting the fæces of the same patient by Fischer's bicarbonate method and with methyl alcohol and hydrochloric acid the presence of small quantities of hæmatoporphyrin similar to that extracted by Fischer from a similar source was established.

S. S. Z.

The Action of Strophanthin on Colloids. GEORG PIETRKOWSKI (*Biochem. Zeitsch.*, 1919, **98**, 92—104).—The action of strophanthin on optically invisible colloidal gold solutions produces an increase in the number of particles visible under the ultra-microscope. In the case of an hydrophile colloid, such as gelatin, strophanthin inhibits imbibition. These facts, it is suggested, justify the conclusion that the increase in tonus in the cardiac muscles brought about by the action of this drug is due to the shrinking of the surface of the muscle fibres. The above experiments, however, do not explain the specificity of strophanthin. S. S. Z.

Chemistry of Vegetable Physiology and Agriculture

Butylene Glycol Fermentation of Sucrose by Bacteria of the Prodigiosus Group. M. LEMOIGNE (*Compt. rend. soc. biol.*, 1919, **82**, 234—236; from *Chem. Zentr.*, 1919, iii, 198).—In addition to acid and traces of ethyl alcohol and acetaldehyde, $\beta\gamma$-butylene glycol and acetylmethylcarbinol are invariably found among the products of the decomposition of sucrose by different varieties of *B. prodigiosus*. The bacteria, therefore, ferment sucrose in the same manner as those of the group of *B. subtilis*, *B. lactis aerogenes*, and *Staphylococci* (A., 1913, i, 1422). H. W.

The Alkali-forming Bacteria found in Milk. S. HENRY AYERS, PHILIP RUPP, and WILLIAM T. JOHNSON, jun. (*U.S. Dept. of Agriculture*, 1919, Bull. No. 782).—The group of bacteria

studied is defined as consisting of those which produce an alkaline reaction in milk without peptonisation of the casein. This group produced the reaction in five days at 30°. The reaction was not due to ammonia, as ammonia was produced by a few organisms only, and then not until the second week. All the citric acid in the milk was used up, and an amount of carbonate corresponding with about half the citric acid was produced. The chief sources of these organisms were milk, soil, and water. Of the species studied, six were cocci and sixty-two were bacilli; all were non-sporing, and had an optimum temperature of 20—30°.

The action of each organism on certain organic compounds was examined, using cultivations in a sodium ammonium phosphate medium containing the test substance as the only source of carbon. The change in the hydrogen-ion concentration was taken as the measure of the alkalinity produced. It was found that dextrose and galactose were fermented by forty-four cultures, lactose by eleven, saccharose by two, and raffinose by none. Ethyl, propyl, and amyl alcohols were more readily fermented than mannitol and glycerol. The sodium salts of many organic acids were also used, with the result that pyruvic, citric, malic, lactic, succinic, acetic, propionic, butyric, valeric, hexoic, mucic, glyceric, tartaric, malonic, formic, benzoic, and salicylic acids were converted into carbonates, and oxalic and glycollic acids were unacted on. *n*-Butyric, *n*-valeric, and *n*-hexoic acids were first converted into simpler acids. An investigation of the results showed that the organisms took their carbon most readily from the alkyl and primary alcohol groups, provided the primary alcohol was not linked to a carboxyl group. A secondary alcohol group was less easily acted on than a primary. The carboxyl group was not split up. Some experiments were made with urea, uric acid, and hippuric acid, as sources of both carbon and nitrogen, and most of the organisms grew well in these media, as also did the well-known organisms of typhoid, paratyphoid, and dysentery. All the organisms were able to utilise the nitrogen in nitrates and nitrites. J. H. J.

Transformation of Cyanamide into Carbamide by the Microbes of the Soil. P. MAZÉ, VILA, and M. LEMOIGNE (*Compt. rend.*, 1919, **169**, 921—923).—It is shown that numerous common species of bacteria abundant in all soils in a good state of cultivation can grow in the presence of cyanamide at a concentration of 1 in 1000, and are capable of rapidly converting the cyanamide into carbamide. W. G.

Solubility of Sparingly Soluble Silver Salts Demonstrated by their Nucleus-destroying Action. H. BECHHOLD (*Kolloid Zeitsch.*, 1919, **25**, 158—161).—*Staphylococcus* cultures in agar-jelly were partly covered with filter paper which had been coated with various sparingly soluble silver salts and left for four days in the dark at the ordinary temperatnre. The preparation was then placed in an incubator for forty-eight hours, and the area was

measured which was entirely free from the micro-organism. It is shown that the areas are practically proportional to the solubility of the salt employed. The experiments were carried out with metallic silver and the oxalate, oxide, carbonate, chromate, chloride, cyanide, thiocyanate, bromide, iodide, and sulphide. Similar experiments were carried out with metallic silver and silver chloride, but using cultures of various micro-organisms, and from the area of the free space deductions are drawn as to the resistance of these organisms to silver and silver chloride. In the case of metallic silver *B. pyocyaneus* is absolutely unacted on, and then follow in decreasing order of resistance, *B. coli*, the organism of swine erysipelas, *Staphylococcus*, paratyphoid, typhoid, and *B. proteus*. In the case of silver chloride the order is entirely different, the organism of swine erysipelas being most resistant, and this is followed in order by *B. pyocyaneus*, *Staphylococcus*, *B. proteus*, *B. coli*, paratyphoid and typhoid. Except in the case of the organism of swine erysipelas silver chloride is much more poisonous than metallic silver.

J. F. S.

Further Experiments on the Correlative Formation of Acetaldehyde and Glycerol by the Scission of Sugar, and New Contributions to the Theory of Alcoholic Fermentation. CARL NEUBERG and ELSA REINFURTH (*Ber.*, 1919, **52**, [*B*], 1677–1703. Compare A., 1914, i, 118).—As the result of the many investigations carried out by Neuberg and his co-workers in recent years, the following representation of the processes occurring in alcoholic fermentation is given:

I. $C_6H_{12}O_6 - 2H_2O = C_6H_8O_4$, the aldol of methylglyoxal

II. $C_6H_8O_4 = 2CH_2{:}C(OH){\cdot}CHO$ or $2CH_3{\cdot}CO{\cdot}CHO$.

III. $CH_2{:}C(OH){\cdot}CHO + H_2O$ ... H_2 ... Glycerol +
$+$ (H₂ over O) $=$
$CH_2{:}C(OH){\cdot}CHO$ ... O ... Pyruvic acid.

IV. $CH_3{\cdot}CO{\cdot}CO_2H = CO_2 +$ Acetaldehyde.

V. $CH_3{\cdot}CO{\cdot}CHO$ ... O ... Pyruvic acid +
$+$ (O over H₂) $=$
$CH_3{\cdot}CHO$ ... H_2 ... Ethyl alcohol.

According to this scheme, methylglyoxal and its corresponding acid, pyruvic acid, are intermediate compounds, and glycerol and acetaldehyde by-products in fermentation. The fact that methylglyoxal may be obtained from sugar by means of quite mild, alkaline agents (A., 1913, i, 1155) is suggestive, and led the authors to investigate the fermentation of sugar in the presence of such substances, especially as it had already been found that the activity of zymase is not impaired by such alkaline compounds (A., 1915, i, 1043). Preliminary experiments showed that the by-products, acetaldehyde and glycerol, become the chief products if sodium sulphite is the agent added (A., 1917, i, 502). This was explained by the formation of the very stable bisulphite compound (A., 1918,

i, 517), the *corresponding* compounds of dextrose or pyruvic acid being so easily dissociated that the reaction is *not stopped until* the acetaldehyde stage is reached. Owing to the arrest of the further reduction of the aldehyde, the available hydrogen must attack some other substance, leading, according to the above theory, to increased production of glycerol. This is now known to be actually the case, having by other workers been applied to the technical production of glycerol. In Neuberg's experiments it was found that for every molecule of acetaldehyde produced there is also one molecule of glycerol, the maximum yield of aldehyde being about 73%, and of glycerol about 70%, of that required by the equation $C_6H_{12}O_6 = CH_3{\cdot}CHO + C_3H_5(OH)_3 + CO_2$.

An important confirmation of this theory of the action of the alkaline sulphite is the fact that neutral, insoluble sulphites, like those of calcium, magnesium, and zinc, and mixtures of sodium sulphite with phosphoric acid or sodium dihydrogen phosphate (that is, actually a feebly acid mixture) influence the course of the fermentation in the same way. In fact, the use of calcium sulphite is to be preferred in all such studies. Furthermore, the more dilute the solution is, the less marked is the effect of the sodium sulphite, even if the actual quantity present is 300% of the weight of the sugar.

The earlier experiments were performed with top yeast. The same results, at any rate in the presence of calcium sulphite, are given by bottom yeast, dried yeast, or maceration juice. In fact, the production of acetaldehyde (sodium nitroprusside–piperidine test) may be demonstrated in less than half an hour by incubating a mixture of 20 c.c. of 10% sucrose or dextrose, 2 grams of baker's yeast, and 2 grams of calcium sulphite (made from sodium sulphite and calcium chloride).

Some experiments on the fermentation of the trioses in the presence of calcium sulphite are also described. Dihydroxyacetone yields acetaldehyde, but disproportionate amounts of glycerol, sometimes higher than the expected quantities, whilst glyceraldehyde gives no acetaldehyde at all. J. C. W.

The Course of Alcoholic Fermentation in the Presence of Calcium Carbonate. JOHANNES KERB (*Ber.*, 1919, **52**, [*B*], 1795—1800).—Fernbach and Schön (A., 1914, i, 237, 910) reported the production of a large amount of calcium pyruvate during the fermentation of dextrose or invert-sugar in the presence of calcium carbonate, which seemed incredible to the author, since he found that pyruvic acid and its salts are more rapidly fermented by yeast than sugar itself (A., 1913, i, 1026). He has therefore tested the question, and finds that the production of alcohol by pure cultures of yeast is quite normal, and that no trace of a pyruvate is present in the soluble calcium salts formed. These consist of the sulphate, phosphate, hydrogen carbonate, and acetate. The only effect is that the yield of acetaldehyde and acetic acid is slightly greater. It is probable that Fernbach and Schön used an impure ferment which

produced a lactate and then pyruvate, that is, the normal alcoholic fermentation was very much suppressed. J. C. W.

The Course of Alcoholic Fermentation in an Alkaline Medium. II. Fermentation with Living Yeast in Alkaline Solutions. CARL NEUBERG and JULIUS HIRSCH (*Biochem. Zeitsch.*, 1919, **96**, 175—203. Compare A., 1917, i, 502).—In the fermentation of sugar by living yeast in the presence of sodium hydrogen carbonate a portion of the acetaldehyde which is formed as an intermediate product is not reduced to alcohol, but is converted into an equimolecular mixture of acetic acid and alcohol. An amount of glycerol equivalent to this portion of acetaldehyde is simultaneously produced. S. S. Z.

The Mechanism of the "Fixation" Method in the Degradation of Sugar into Acetaldehyde and Glycerol. The Correlation of Acetaldehyde and Glycerol during the Entire Process of Fermentation, the Time Factor in this Process and its Relation to Alcoholic Fermentation. CARL NEUBERG and JULIUS HIRSCH (*Biochem. Zeitsch.*, 1919, **98**, 141—159).—At every stage during the process of fermentation of sugar in the presence of sodium sulphite, acetaldehyde and glycerol are produced in equimolecular proportions. As ethyl alcohol and carbon dioxide are also produced independently at the same time in equivalent proportions, the fermentation process can be followed by estimating the alcohol and aldehyde at the various stages. S. S. Z.

Utilisation of Amides by Yeast. PIERRE THOMAS (*Ann. Inst. Pasteur*, 1919, **33**, 777—806).—Under suitable conditions, yeasts are capable of utilising carbamide, and to a lesser extent acetamide, as their source of nitrogen during the fermentation of sugar. Slight utilisation of propionamide and butyramide was indicated. The mechanism of this utilisation is not clear. Although all the experiments with carbamide indicate that the organic nitrogen is converted into ammoniacal nitrogen before utilisation, it was not possible to detect any urease or other such hydrolysing ferment either in the culture liquids or in the expressed cellular juice of the yeast. W. G.

Influence of Zinc Chloride on the Alcoholic Fermentation of Living and Killed Yeast. S. KOSTYCHEV and L. FREY (*J. Russ. Bot. Soc.*, 1916, **1**, 39—47; from *Physiol. Abstr.*, 1919, **4**, 416).—Zinc chloride causes a production of acetaldehyde in "hefanol" and dry yeast, but not in living yeast. An important part of fermented sugar forms some compounds the structure of which is not yet known; acetaldehyde is formed only in presence of sugar; the quantity of carbon dioxide exceeds the quantity of alcohol. J. C. D.

The Action of Salts of Zinc and Cadmium on the Ferments of Yeast. S. KOSTYCHEV and ZUBKOVA (*J. Russ. Bot. Soc.*, 1916, **1**, 47—56; from *Physiol. Abstr.*, 1919, **4**, 416).—The formation of acetaldehyde by dry yeast under the action of zinc salts depends on the influence of the zinc ion; a similar, but more energetic, effect can be produced by cadmium salts in the case of sugar fermentation, but not in the autolysis in water.

In the presence of cadmium salts, sucrose and lævulose produce a much larger quantity of acetaldehyde than dextrose. The reduction activity of yeast is very strongly inhibited by cadmium; the proteolytic ferments, on the contrary, show no change in their power either in the presence or absence of that metal. Salts of calcium, magnesium, strontium, mercury, aluminium, and antimony give no effects analogous to those produced by zinc and cadmium.

J. C. D.

The Decomposition of Lactic Acid by Killed Yeast. V. I. PALLADIN and D. A. SABYNIN (*Bull. Acad. Sci. Petrograd*, 1916, 187—194; from *Physiol. Abstr.*, 1919, **4**, 417).—Lactic acid is decomposed by killed yeast in the presence of methylene-blue, and in a lesser degree in the presence of pyruvic acid; in the latter case, acetaldehyde is not produced. The authors believe that acetaldehyde plays a rôle of an acceptor of hydrogen, and is transformed into alcohol. Further work is necessary to determine whether lactic acid is an intermediate compound in the course of alcoholic fermentation. J. C. D.

The Influence of Alcohol and Methylene-blue on the Evolution of Carbon Dioxide by Killed Yeast. V. I. PALLADIN and E. I. LOVCHINOVSKAIA (*Bull. Acad. Sci. Petrograd*, 1916, 253; from *Physiol. Abstr.*, 1919, **4**, 416).—The experiments on the capacity of killed yeast to oxidise alcohol to carbon dioxide in the presence of an hydrogen acceptor failed. J. C. D.

The Yeast Saccharomyces Thermantitonum. HANS VON EULER and INGVAR LAURIN (*Biochem. Zeitsch.*, 1919, **97**, 156—170).—The inversion capacity, the catalase activity, the rate of fermentation at 35° and 40°, and the growth of *Saccharomyces thermantitonum* have been studied. The culture now examined showed certain deviations in its behaviour at the characteristic temperatures from the original culture (1905). It is suggested that adaptation may be responsible for this. S. S. Z.

Rôle Played by Water in the Processes of Alcoholic Fermentation and of Respiration of Plants. V. I. PALLADIN (*Rec. d'art. dedié au Prof. C. Timiriazev*, 1916, 1—34; from *Physiol. Abstr.*, 1919, **4**, 426).—The replacement of water, although only partial, by some other solvent, such as glycerol, ethylene glycol, formamide, pyridine, or ethyl alcohol, inhibits strongly the activity of zymase, carboxylase, and reductase. In the absence

of water there is no possibility for action of either ferments of alcoholic fermentation or of those of the anærobic phase of respiration. Water is assimilated during respiration, and is used for an anærobic oxidation of dextrose. The total carbon dioxide excreted at the time of respiration is of anærobic origin. Hydrogen, which is formed in higher plants during their respiration as a result of the anærobic decomposition of dextrose, is temporarily adsorbed by some special hydrogen acceptors (respiratory pigments). The total amount of oxygen adsorbed at the time of respiration is used exceptionally to oxidise hydrogen bound by hydrogen acceptors. Water produced during respiration is of anærobic origin. Anthocyanins play no immediate rôle in the respiratory process. Peroxydases serve for the formation of water and of pigments. The respiratory pigments play a rôle of mediators between the products of the anærobic decomposition of dextrose and peroxydases. The oxidation of chromogens follows the scheme of a moist auto-oxidation. Oxygen adsorbed at the time of respiration acts only as a hydrogen acceptor. Thus the majority of cases, if not all, in which the assimilation of atmospheric oxygen is accepted are in reality cases of an oxygen assimilation from water.

J. C. D.

Apparatus for the Study of Photosynthesis and Respiration. W. J. V. OSTERHOUT (*Bot. Gaz.*, 1919, **68**, 60—62).— A very simple apparatus is described and figured in the original, by means of which the air in a closed space, in which is present a branch or twig with green leaves and with the stem dipping into water, is caused to circulate through a solution of an indicator sensitive to carbon dioxide. By means of this the variation in the carbon dioxide concentration in the closed space may be followed, whilst the process of photosynthesis or the process of respiration is proceeding in the plant.

W. G.

Carbon Dioxide and Plants. II. E. REINAU (*Chem. Zeit.*, 1919, **43**, 449—451, 489—491, 509—512, 524—525. Compare Klein and Reinau, A., 1914, i, 789).—From a lengthy review of the available data concerning the amount of carbon dioxide in the air, its fluctuations, and its effect on the growth of plants, the author is led to the following conclusions. Brown's theory of the internal pressure of carbon dioxide in plants containing chlorophyll is extended to the phenomena of assimilation under natural climatic conditions, and a mathematical expression is developed which takes into consideration the effect both of water and carbon dioxide on the growth of plants. The differences in concentration of these substances within and without the plant are regarded as differences of tension, the value of which appears to depend mainly on temperature and atmospheric humidity. Under climatic conditions, the amount of assimilation by green plants is not proportional to the absolute carbon dioxide content of the air, but to the difference in tension. The internal pressure of carbon dioxide

depends on the temperature, with rise of which it increases, and also on the illumination, with increase of which it falls. The two functions are explained by Willstätter's conception of the dual nature of chlorophyll; the presence of magnesium in the latter enables it to form a dissociating compound with carbon dioxide resembling a bicarbonate, whilst its chromophoric complex conditions its sensitiveness to light. The actual value of the carbon dioxide tension difference depends on the capacity of the air to receive water vapour, and therefore indirectly on the temperature, and this is explained by the close connexion which exists between the utilisation of the carbon, water, and salts within the plant.

The *generally accepted idea that the plant is only able to utilise* 0·5—1·0% of the light energy falling on it appears to be erroneous. Assimilation of carbon must proceed simultaneously with the evaporation of water; the latter process requires from 25·5% (in full sunlight) to 92·3% (in shade) of the energy derived from the sun by the leaf; the chlorophyll, in virtue of the power of selective light absorption exhibited by its chromophoric complex, converts about 7% of the light energy into chemical energy, and can utilise this amount completely in experimental cases and to the extent of 10—33% under climatic conditions.

The carbon dioxide content of the atmosphere is regulated by the activity of terrestrial green plants and of the sea on the one hand, and by that of humus (edaphon) on the other; this is rendered probable by the extreme sensitiveness of plants to alteration in the tension of carbon dioxide and by the fact that the action of green plants and "edaphon" is so nicely balanced that the actual quantity of carbon dioxide in the atmosphere is the expression of the dynamic equilibrium of the results of these two factors. Consequently, the absolute carbon dioxide content of the atmosphere is not a measure of the amount of carbon dioxide available for vegetation, but represents the proportion which cannot be lessened by plants under average conditions. It is conceivable that cases could arise in the open in which the plant suffers from too little carbon dioxide; the agricultural aspect of this possibility and the means of preventing it are discussed in the original paper, as is also the beneficent effect of an increased concentration of carbon dioxide on diseased plants.

Schlœsing's theory of the regulation of the carbon dioxide content of the atmosphere by the ocean is regarded as not sufficiently firmly established, and as a partial aspect of the actual case.

H. W.

Formation of Inositol and Hexaldehyde in the Light. P. R. Kögel (*Biochem. Zeitsch.*, 1919, **97**, 21—23).—A theoretical paper. Inositol and hexaldehyde in the plant are formed by photosynthesis according to the following scheme:

Tetrahydroxyethylene ⟶
hydrate of hexaketohexamethylene ⟶ inositol.
Inositol ⟶ *cyclo*hexanone ⟶ hexaldehyde.

In a previous communication (A., 1919, i, 471) the author pu forward a scheme in which he considered that tetrahydroxyethylen was an intermediate product in the formation of formaldehyde fron carbon dioxide. S. S. Z.

The Hydrocyanic Acid Question. L. ROSENTHALER (*Schweiz. Apoth. Zeit.*, 1919, **57**, 267—270, 279—283, 295—297, 307—313 324—329, 341—346; from *Chem. Zentr.*, 1919, iii, 274—275).—Dezani's supposed conversion of hydrocyanic acid into ammonia by the sap of plants is erroneous; its production is due to the hydrolysis of the cyanohydrins of sugar, and occurs under conditions which could not obtain in the plant. The author has been unable to detect any formation of ammonia from hydrocyauic acid in the cold, unchanged, and therefore acid, sap from the leaves of *Cornus sanguinea*, *Sambucus nigra*, etc. The presence of hydrocyanic acid, which is important from the point of view of Treub's hypothesis of nitrogen assimilation, has been detected with certainty in about 360 varieties in 148 species and 41 families; the varieties are enumerated in the original memoir, and particular reference is made to the distribution of the acid in the various parts of the plant. Generally, the presence of alkaloids and ethereal oils appears to be incompatible with the presence of hydrocyanic acid. H. W.

Histological Investigations of Oxydases and Peroxydases. G. MARINESCO (*Compt. rend. soc. biol.*, 1919, **82**, 258—263; from *Chem. Zentr.*, 1919, iv, 173).—The presence of oxydases in the cells of various tissues can be detected histologically by the blue coloration of the cell granula when treated with solutions of α-naphthol and *p*-phenylenedimethyldiamine. Since, however, fatty substances give a coloration with this reagent, a control with osmic acid and Nile-blue must be made in order to obtain an estimate of the actual amount of oxydase present. The presence of peroxydase can be detected by Perl's iron reaction, since its action is connected with the presence of this metal. H. W.

The Constituents of Wood which give Colour Reactions. III. H. WICHELHAUS (*Ber.*, 1919, **52**, [*B*], 2054—2056. Compare A., 1916, i, 874; 1918, i, 151).—The active constituents have been removed from the distillates by extraction with ether and purified by distillation under greatly diminished pressure; two fractions, b. p. 88°/0·4 mm. and 95—105°/0·4 mm., are obtained, together with formic acid. Analyses of the fractions give results in agreement with those required by the formulæ $C_{16}H_{22}O_9$ and $C_{16}H_{22}O_{10}$ respectively, which are simply related to the formulæ of brazilin and hæmatoxylin. H. W.

In. **Some Components of Althæa (Marsh Mallow) Root.** IONKAR VON FRIEDRICHS (*Arch. Pharm.*, 1919, **257**, 288—298).—lifferent mallow root contains 1·7% of an oil, consisting of glycerides itic and oleic acids, together with butyric acid and a phyto-

sterol apparently identical with sitosterol; a hydroxy-acid of high molecular weight also appears to be present. The odour of the root is due to a substance of unknown composition, soluble in ether, insoluble in light petroleum, and non-volatile in a current of steam. The root contains a lecithin in which palmitic and oleic acids occur, and the base of which consists of choline. The sugar present is principally sucrose, of which the root contains 10·2%, the proportion of invert sugar being only 0·78%. The mucilage has the formula $(C_6H_{10}O_5)_n$ and consists of glucosan (64%) and xylan. No galactose is present, but another saccharo-colloid, giving *d*-galactose on hydrolysis, is found. T. H. P.

The Saponins of Chenopodium quinoa, Euphorbia helioscopia (Tithymatus helioscopius), Euphorbia Peplus, and Mercurialis perennis. M. GONNERMANN (*Biochem. Zeitsch.*, 1919, **97**, 24—40).—Preparations of the acid and neutral saponins of these plants have been investigated for their activity by hæmolysis of sheep's and human corpuscles. The titres are given. S. S. Z.

The Saponin in Fenugreek Seeds. H. E. WUNSCHENDORFF (*J. Pharm. Chim.*, 1919, [vii], **20**, 183—185).—The saponin may be isolated by extraction with alcohol and precipitation by ether from the alcoholic solution; the substance consists of a semi-crystalline, white powder, m. p. 214—215°. On acid hydrolysis it yields a sapogenin and dextrose. W. P. S.

Endothia Pigments. II. Endothin-red. L. E. SANDO (*Amer. J. Bot.*, 1919, **6**, 242—251; from *Physiol. Abstr.*, 1919, **4**, 350).—This pigment was obtained from the alcoholic extract of cultures of *Endothia fluens* grown on rice. Analysis and properties indicate a formula C_7H_5O and its probable relationship to the catechol group. J. C. D.

Chemistry of Heterotropic Phanerogams. JULIUS ZELLNER (*Monatsh.*, 1919, **40**, 293—311).—A further extension and elaboration of the author's work on this subject (compare A., 1914, i, 913). Analysis of the ash of *Neottia nidus avis*, *Monotropa hypopitys*, *Cuscuta europaea*, *Lathraea squamaria*, and *Orobanche gracilis* discloses a high percentage of potassium, medium or small amounts of calcium, normal quantities of magnesium, and varying amounts of manganese which are probably connected with the presence of very active oxydases. The ratio of soluble nitrogen to total nitrogen is relatively high, but not the same for all parts of the plant. The question of the osmotic pressure of the cell sap is discussed, but, unfortunately, direct measurement is not yet possible. On various grounds, the author is led to the conclusion that heterotropic plants poor in chlorophyll are richer in osmotically active substances than are the green plants. Analyses show that in all probability the concentrations of cell sap in the parasite and host do not differ widely, in spite of the frequently great differences in water content.

The paper concludes with a critical review of the results obtained by the author and others in the study of the biochemistry of heterotrophic phanerogams. H. W.

The Honey of the Poplar. Georges Tanret (*Compt. rend.* 1919, **169**, 873—874).—The sugary exudation on the leaves of *Populus nigra* contains three sugars, namely, melizitose, dextrose and lævulose. W. G.

The Colouring Matter of the Red Pea Gall. Maximilian Nierenstein (T., 1919, **115**, 1328—1332).

Function of Oxalic Acid in the Plant. The Enzymic Degradation of Oxalic Ions. Markus Staehelin (*Biochem. Zeitsch.*, 1919, **96**, 1—50).—Various plants have been examined and found to contain an enzyme which acts on oxalic ions. It appears that the enzyme is fairly widespread in the plant kingdom, being also present in non-acid plants. It is found in most parts of the plant. The enzyme, which is an oxydase, also functions as a carboxylase converting a part of the oxalic ions into carbon dioxide. Its optimum temperature is 30—40°, and it is destroyed on boiling. It is active under ærobic conditions. In the leaves of *Rumex* the degradation of the oxalic ions proceeds according to the formula of a unimolecular reaction, whereas in the powdered leaves of *Helianthus* it functions in accordance with the law of autocatalysis. Its activity is retarded with increased concentration of oxalates. S. S. Z.

Chemical Composition of Natural and Polished Italian Rice. I. Giovanni Issoglio (*Atti R. Accad. Sci. Torino*, 1917—1918, **53**, 423—436).—The analytical results obtained by the author show that polished rice is very poor in ash and also in total phosphoric oxide, the phytin phosphoric oxide being reduced to a minimum. T. H. P.

Chemical Composition of the Residues from the Treatment of Rice. II. Giovanni Issoglio (*Atti R. Accad. Sci. Torino*, 1918—1919, **54**, 440—451).—The rice offals derived from the husk are all very poor in nutritive substances. The residues obtained by removal of the outer cortical layers of the corns are, however, very rich in organic and inorganic phosphorus compounds, fats, and proteins, and contain phytin and vitamines. A third class of residues, composed of small, detached fragments of rice, together with foreign seeds, contains (1) products such as rice embryos, etc., which are used only as cattle feed, and (2) products which are similar in chemical composition to rice and are of value as human food. The results emphasise the necessity of reducing to a minimum the treatment to which rice is subjected. T. H. P.

Organic Chemistry.

Action of Selenyl Chloride on Unsaturated Compounds. ARNO MÜLLER (*Chem. Zeit.*, 1919, **43**, 843).—Preliminary qualitative experiments show that selenyl chloride combines with unsaturated hydrocarbons and ketones to form well-defined, crystalline additive *compounds* which are somewhat unstable towards light and air, and are readily decomposed by boiling water into selenyl chloride and the corresponding hydrocarbon or ketone. Thionyl chloride also unites with olefinic substances to give small amounts of deeply coloured additive products, but the reaction is generally uncontrollably violent, and the formation of by-products cannot be avoided. H. W.

Removal of Aromatic Hydrocarbons from Mineral Oils by means of Trioxymethylene-sulphuric Acid. JENÖ TAUSZ (*J. pr. Chem.*, 1919, [ii], **99**, 276—280).—Nastkujoff's formolite reaction (A., 1904, i, 801) for aromatic hydrocarbons is also shown by diolefines, such as methyl- and dimethyl-butadienes, which contain conjugated double bonds, owing to their condensation to ring compounds under the influence of sulphuric acid. On the other hand, the reaction is limited in the case of aromatic hydrocarbons to those containing a hydrogen atom in the nucleus, since hexamethyl- and hexaethyl-benzenes do not answer to it. Aromatic hydrocarbons are usually completely removed from mineral oils by this method, or by Herr's modification (A., 1910, ii, 904) only after a repetition of the treatment, owing to gradual dilution of the sulphuric acid. The author overcomes this difficulty by the use of trioxymethylene in place of formaldehyde solution or methylal. [See, further, *J. Soc. Chem. Ind.*, 1920, February.] J. K.

Action of Fluorine on Organic Compounds. BURR HUMISTON (*J. Physical Chem.*, 1919, **23**, 572—577).—The action of fluorine on organic compounds is usually violent, leading to decomposition. Saturated hydrocarbons are ignited with incandescence and formation of free carbon, carbon fluorides, and hydrogen fluoride. "Filtchar" charcoal is attacked at the ordinary temperature, a gas, non-liquefiable at $-80°$, being the chief product, accompanied by carbon tetrafluoride and tetrafluoroethylene (compare Moissan, A., 1890, 55). Selenium also yields as chief product a gas, which escapes liquefaction at $-80°$ (compare Prideaux, T., 1906, **84**, 316). Acetone is ignited by pure fluorine, whilst, in presence of an indifferent gas, charring takes place and some tetrafluoroethylene is produced. An indefinite product containing some carbonyl chloride is obtained from chloroform. Carbonyl chloride appears to be unattacked at 6°, but apparently some carbonyl fluoride is

produced at 200°. No evidence could be obtained of a reaction with carbon monoxide. Carbon tetrachloride is only slightly attacked at the ordinary temperature, but tetrachloroethylene gradually blackens even at 0°, hexachloroethane being among the products. J. K.

Tetrachlorodinitroethane. W. L. ARGO, E. M. JAMES, and J. L. DONNELLY (*J. Physical Chem.*, 1919, **23**, 578—585. Compare Biltz, A., 1902, i, 417).—Tetrachlorodinitroethane is very soluble in liquid nitrogen tetroxide, and has pronounced toxic and lachrymatory properties. The optimum temperature for its production from dry liquid nitrogen tetroxide and tetrachloroethylene is 80°. [See, further, *J. Soc. Chem. Ind.*, 1920, 82A.] J. K.

Preparation of Ethyl Alcohol. ELEKTRIZITÄTSWERK LONZA (Brit. Pat. 134521).—In the catalytic reduction of acetaldehyde to ethyl alcohol by means of hydrogen, the excess being returned to the operation by a circulating device (Brit. Pat. 120163), the production of ethyl ether as a by-product, and the gradual poisoning of the catalyst by the decomposition products of acetaldehyde, are avoided by circulating with the hydrogen an amount of oxygen not exceeding 0·3%. The temperature of the reaction chamber is maintained between 90° and 170° by cooling, or preferably by using the hydrogen in such excess that it absorbs and removes the superfluous heat of the reaction. Whereas without the use of oxygen the yield of alcohol fell after thirty hours nearly to zero, an average yield of 95% of the alcohol theoretically possible was obtained in a run extending over two hundred and eleven hours, in which 0·15% of oxygen was used. This beneficial effect of the oxygen cannot be attributed to the complete oxidation of carbon monoxide, methane, etc., to the presence of which the injurious effect on the catalyst is ascribed. G. F. M.

Melissyl Alcohol and Melissic Acid. A. HEIDUSCHKA and M. GAREIS (*J. pr. Chem.*, 1919, [ii], **99**, 293—311).—The formula for melissyl alcohol has been considered by some workers to be $C_{30}H_{61}\cdot OH$, by others $C_{31}H_{63}\cdot OH$. The authors have therefore prepared a series of derivatives of melissyl alcohol from carnauba wax and from beeswax, and confirmed the view of Schwalb (A., 1885, 962) that the alcohols from these sources differ. The former has the formula $C_{30}H_{61}\cdot OH$, whilst that of the latter is $C_{31}H_{63}\cdot OH$. The melting points of their respective derivatives were as follows (those of carnauba melissyl alcohol being quoted first): *acetates*, 74° and 70°; *benzoates*, 69·5° and 66°; *phthalates*, 82° and 81·5°; *monochloroacetates*, 79·5° and 74°; *phenylurethanes*, 98° and 96°; *chlorides*, 67° and 65°; *bromides*, 68° and 67°; *iodides*, 69·5° and 68°. Carnauba melissyl alcohol on oxidation by Hell's process (A., 1884, 1433) gave a melissic acid, $C_{30}H_{60}O_2$, m. p. 90° (lead salt, m. p. 118°), whilst the acid, $C_{31}H_{62}O_2$, from beeswax had m. p. 88·5° (lead salt, m. p. 115°). The latter acid was also obtained by

hydrolysis of carnauba melissyl cyanide, which in an impure condition melted at 75°.

Stürcke's observation (A., 1884, 1280) that carnauba melissyl alcohol is accompanied by an alcohol, $C_{27}H_{56}O$, m. p. 76°, was also confirmed.
J. K.

Phytochemical Reduction of Ketones. Biochemical Preparation of Optically Active Secondary Alcohols. C. Neuberg and F. F. Nord (*Ber.*, 1919, **52**, [*B*], 2237—2248).—The authors find that the phytochemical reduction of the ketonic group is frequently possible both with aromatic and aliphatic ketones, and leads to the production of the corresponding secondary alcohols. Hydrogenation is more difficult than with the aldehydes, since it proceeds more slowly and less completely, and also requires more energetic conditions. The biological nature of the process is shown by the fact that the secondary alcohols are optically active, an asymmetric carbon atom being developed during the process. They have been isolated in the chemically pure condition, but the yields are poor (about 10%) and a considerable portion of the original material remains unattacked, and is subsequently removed by treatment with sodium hydrogen sulphite or hydrazine bases. They are not optically pure. Acetaldehyde is invariably also formed, the oxidative production of which is probably the complementary process of the hydrogenation of the ketone.

The mixtures were generally made from conductivity water (2 litres) at 35—40°, sucrose (200 grams), yeast (200 grams) and the ketone (10—15 grams), and fermentation was allowed to proceed for three to six days, frequently followed by a second addition of sucrose and yeast and renewed fermentation. In this manner methyl ethyl ketone yielded *d*-methylethylcarbinol, b. p. 99—100°, $[\alpha]_D$ +3·34°, methyl *n*-propyl ketone gave *d*-methyl *n*-propylcarbinol, b. p. 117—119°, $[\alpha]_D^{18}$ +6·3°, D^{16} 0·810, methyl *n*-hexyl ketone yielded *d*-methylhexylcarbinol, b. p. 177—179°, $[\alpha]_D^{18}$ +2·85°, whilst *d*-methylnonylcarbinol, b. p. 228—229°, $[\alpha]_D^{16}$ +2·95°, and *l*-phenylmethylcarbinol, b. p. 202—204°, $[\alpha]_D^{16}$ −8·01°, were prepared from methyl nonyl ketone and acetophenone respectively.
H. W.

Phytochemical Reduction of Diketones. C. Neuberg and F. F. Nord (*Ber.*, 1919, **52**, [*B*], 2248—2254. Compare preceding abstract).—The authors find that diacetyl can be readily hydrogenated by biochemical methods, and that *l*-βγ-butylene glycol is produced in yield which is regarded as satisfactory when the difficulties of isolation are taken into consideration; the optical activity of the product is the more remarkable, since Harden and Walpole have found that the action of bacteria on a series of carbohydrates leads to a mixture of the racemic and meso-forms of the glycol. Under similar circumstances, benzil yields benzoin, which in the main is optically inactive, but which contains small amounts of *l*-benzoin. Attempts to reduce benzil or benzoin to the corresponding glycol were unsuccessful.
H. W.

Addition Catalysis by means of Diethyloxonium Salt $\frac{Et}{Et}>O<\frac{H}{R}$. OSSIAN ASCHAN (*Medd. K. Vetenskapsakad. Nob Inst.*, 1919, **5**, No. 8, 1—32).—Reference is first made to the use ethereal solutions of hydrogen chloride in the synthesis of hyd chlorides in the terpene series (compare A., 1916, i, 51), and it pointed out that without the use of ethyl ether as catalyst tertia pinene hydrochloride (*Öfvers. Finska Vet-Soc. förh.*, 1914—191 **57**, [A], No. 1) could not have been prepared. The results th obtained with the ether-additive product of hydrogen chloride l the author to investigate the addition of water to unsaturat compounds by means of a mixture of absolute ether and sulphur acid monohydrate. When this mixture is made there is a lar development of heat, and when the two components are in equiv lent quantities the resulting mixture is much more viscous th the sulphuric acid. It is concluded that diethyloxonium sulphat $OHEt_2\cdot O\cdot SO_2\cdot OH$, is formed, although neither it nor a salt cou be isolated.

The method of experiment was generally to dissolve the su phuric acid monohydrate in the molecular quantity of ethyl ethe or, if necessary, in an excess of ether, well cooling meanwhile, an then add the unsaturated compound in small portions at a tim again well cooling. In some experiments a further quantity water was added to the sulphuric acid monohydrate. After keepi for some time the resulting mixture was poured into an excess sodium carbonate solution and the products isolated by steam disti lation and subsequent fractionation.

The normal reaction would be represented by the equations:

$$\frac{Et}{Et}>O<\frac{H}{O\cdot SO_2\cdot OH} + R<\frac{CH}{\overset{\|}{CH}} = Et_2O + R<\frac{CH_2}{\overset{|}{CH}\cdot O\cdot SO_2\cdot OH(Na)} \quad \text{an}$$

$$R<\frac{CH_2}{\overset{|}{CH}\cdot O\cdot SO_2\cdot ONa} + H_2O = R<\frac{CH_2}{\overset{|}{CH}\cdot OH} + NaHSO_4,$$

the alcohol being produced, but in some cases, possibly when th reaction mixture is poured into the sodium carbonate solution fission of water takes place with reproduction of the original com pound or an isomeride; di- and poly-terpenes may also be produced

Camphene hydrate and santenol, which are among the lesse sensitive alcohols, are the main products of reaction from camphen and santene, but some of the original substances are re-formed either as such or as diterpenes. The more sensitive alcohols, whic should result from such substances as pinene, nopinene, etc., ar not produced, either the original compound being re-formed or els a polymerisation product obtained. In the case of β-methyl-Δ^{β}-butylene, the dipolymeride, diamylene, is readily obtained in an almost pure condition, together with smaller quantities of tertiary *iso*amyl alcohol.

Absolute ethyl ether and colourless concentrated nitric acid, when mixed in small quantities, give a mixture, which is stable for a

short time. Diethyloxonium nitrate may be present in such a mixture. T. S. P.

Kephalin. VII. The Glycerophosphoric Acid of Kephalin. P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1919, **40**, 1—16). —The generally accepted formula of kephalin presumes the existence of glycerophosphoric acid in the molecule, but the experimental evidence produced so far in support of this supposition is not convincing. The presence of glycerol in kephalin has been satisfactorily demonstrated (Foster, A., 1915, ii, 493). Theoretically, there are only two alternative ways in which glycerol may be attached to phosphoric acid, either directly with the formation of glycerophosphoric acid, or indirectly with the glycerol attached to the aminoethyl alcohol. If the latter condition existed, the amino-group of the kephalin molecule would not be free. Since it has been experimentally shown that the amino-group is free, it follows that the presence of glycerophosphoric acid in kephalin could have been accepted before the substance was actually isolated.

The glycerophosphoric acid isolated from the hydrolysis of kephalin possesses an optical rotation of the same magnitude as the acid from lecithin, namely, $[\alpha]_D^{20} = -0.69°$. This work establishes the fact that glycerophosphoric acid exists in kephalin, and that the acid is identical with that present in lecithin. The crude barium glycerophosphate from kephalin shows dextrorotation, which may account for the statement made by Fränkel and Dimitz (A., 1909, i, 870) that the glycerophosphoric acids present in lecithin and kephalin are optical isomerides. The authors have now shown, however, that on purification the dextrorotation is lost. It is probably due to admixture of the barium glycerophosphate with a dextrorotatory product of intermediary hydrolysis. The authors are unable to confirm the observations of Willstätter and Lüdecke, who stated that the optical rotation of the glycerophosphoric acid from lecithin differs according to the mode of preparation. The maximum rotation for the glycerophosphoric acid from lecithin is found to be $[\alpha]_D^{20}$ $-0.74°$, a value lower than that recorded by Willstätter and Lüdecke (A., *1904*, i, 1067). J. C. D.

The History of Zeise's Mercaptan and its Name (1833). PAUL DIERGART (*J. pr. Chem.*, 1919, [ii], **99**, 281—292).—Historical. J. K.

Preparation of Ethylene Ethylidene Disulphide. OSKAR MATTER (D.R.-P. 313650; from *Chem. Zentr.*, 1919, iv, 617—618). —When the amorphous ethylene sulphides, $(C_2H_4S)_x$, m. p. 145° and 176° respectively (prepared by the action of ethylene chloride or bromide on aqueous or alcoholic solutions of alkali sulphides), are heated almost to dull redness in the absence of air, the main portion distils as *ethylene ethylidene sulphide*, leaving only an unimportant charcoal-like residue. Decomposition occurs more smoothly when a solid substance, such as a metallic sulphide, is

added to the ethylene sulphide and when a slow current of hydr gen sulphide is sent through the apparatus. After being froze out, the crude material is purified by passage through a tube loose packed with fragments of porous pot and heated at about 300 The vapours are collected in a well-cooled receiver. Ethyle ethylidene disulphide, after being shaken with aqueous alkali, obtained as an almost colourless liquid, b. p. 172—173°, which is good solvent for organic substances and may serve as a basis f pharmaceutical preparations. H. W.

Volatility with Steam of Lower Fatty Acids in Dilut Aqueous Solution. EDGAR J. WITZEMANN (*J. Amer. Chem. So* 1919, **41**, 1946—1951).—The volatility in steam of formic acid, acet acid, propionic acid, and butyric acid has been examined by disti ling equivalent solutions (about 1%) and analysing the distillat The volatility is shown to increase with increasing molecular weigh Thus the first fraction (20 c.c.) to distil over contains 6·92% of t acetic acid, 3·94% of the formic acid, 12·4% of the propionic aci and 19·5% of the butyric acid, whilst the residue (15 c.c.), aft distillation of 180 c.c., contains 36·8% of the formic acid, 18·6% the acetic acid, 5·7% of the propionic acid, and 1·4% of the butyr acid. This behaviour is explained as due to the hydration of t acids to form stable complexes, which lower the vapour pressu of the solution. The addition of potassium chloride or magnesiu chloride to solutions of formic or acetic acid increases the volatili of the acids. The increase in volatility depends on the concentr tion of the salt, and also on its nature. Thus 0·5*N*-potassiu chloride has about the same effect as 0·2*N*-magnesium chlorid Using a series of salts in 0·25*M* quantities in formic acid solutio the volatility in steam is increased in every case, the order bei an increasing volatility with decreasing electro-affinity of t metallic ion of the salt for the chlorides of potassium, sodiu barium, strontium, calcium, magnesium, and alumiuium. T chlorides of iron, manganese, and copper are irregular in the action. J. F. S.

The Chlorination of Methyl Formate and Chloroformat V. GRIGNARD, G. RIVAT, and ED. URBAIN (*Compt. rend.*, 191 **169**, 1074—1077. Compare Kling, Florentin, Lassieur, an Schmutz, this vol., i, 8).—Light exerts a marked influence on t chlorination of methyl chloroformate. In diffused light it is on the chloromethyl ester which is formed, bright sunlight being nece sary for the formation of the di- or tri-chloromethyl ester. In ultr violet light the trichloro-ester is easily obtained. The effect temperature is such that up to 110—112° the chlorination pr ceeds smoothly, but at 113—114° it slackens very noticeably an at 117° decomposition begins to take place with the formation carbonyl chloride.

Catalysts, such as ferric chloride, antimony chloride, etc., a beneficial at first in the formation of the dichloromethyl ester, b

when a certain concentration is reached decomposition commences, and may continue indefinitely, as some of the perchloride becomes dissolved in the liquid and continues its action. W. G.

The Chloro-derivatives of Methyl Formate and Methyl Carbonate. V. GRIGNARD, G. RIVAT, and ED. URBAIN (*Compt. rend.*, 1919, **169**, 1143—1147. Compare this vol., i, 8, and preceding abstract).—A study of the properties of the chloromethyl chloroformates and of chloro-derivatives of methyl carbonate.

Chloromethyl chloroformate, $ClCO_2\cdot CH_2Cl$, is a lachrymatory liquid and has b. p. 106·5°, D^{14} 1·456, n_D^{20} 1·42857. Dichloromethyl chloroformate is a lachrymatory liquid, b. p. 46°/62 mm. and 111°, D^{17} 1·558, n_D^{22} 1·44322. Trichloromethyl chloroformate is less lachrymatory but more suffocating than the two preceding esters, and has b. p. 125—126°/748 mm., D^{15} 1·644, n_D^{22} 1·45664.

By moderate chlorination of methyl chloroformate in diffused sunlight *trichloromethyl carbonate*, b. p. 138°, $D^{22\cdot5}$ 1·297, n_D^{20} 1·41160, is obtained as one of the products. *Dichloromethyl methyl carbonate* has b. p. 48—49°/18 mm., D^{17} 1·412, n_D^{20} 1·42852. *Chloromethyl dichloromethyl carbonate*, one of the products of the more intense chlorination of methyl chloroformate, has b. p. 96°/45 mm. and 177—179°, D^{18} 1·553, n_D^{22} 1·45414. Methyl trichloromethyl carbonate has b. p. 59·5—60°/16 mm. and 161—163°, D^{17} 1·525, n_D^{20} 1·44964. s-*Tetrachloromethyl carbonate*, b. p. 83°/19 mm. or 93—94°/20 mm., D^{18} 1·630, n_D^{22} 1·46306, is one of the products of the chlorination of methyl chloroformate in a leaden vessel. By carrying the chlorination still further, hexachloromethyl carbonate, m. p. 79°, is obtained. W. G.

Properties of the Chloromethyl Chloroformates. ANDRÉ KLING, D. FLORENTIN, A. LASSIEUR, and E. SCHMUTZ (*Compt. rend.*, 1919, **169**, 1166—1168).—A study of the physical and chemical properties of the mono-, di-, and tri-chloromethyl chloroformates.

The purest specimen of chloromethyl chloroformate contained 8·6% of the dichloromethyl ester. It had b. p. 52·5—53°/100 mm. and 106·5—107°/700 mm., D^{15} 1·465. It is both lachrymatory and suffocating. It is quantitatively decomposed by water according to the equation $Cl\cdot CO_2\cdot CH_2Cl + H_2O = H\cdot CHO + CO_2 + 2HCl$. With alcohols it gives the corresponding mixed chloromethyl carbonates, and with sodium phenoxide it gives *phenyl chloromethyl carbonate*, b. p. 122—124°/13 mm., D^{23} 1·255. Anhydrous aluminium or ferric chloride decomposes chloromethyl chloroformate at 70°, giving carbonyl chloride.

Dichloromethyl chloroformate has b. p. 54—55°/100 mm. and 110—111°/700 mm., D^{15} 1·560. On hydrolysis it yields carbon monoxide, carbon dioxide, and hydrogen chloride. With alcohols it gives the mixed dichloromethyl carbonates, and with sodium phenoxide *phenyl dichloromethyl carbonate*, m. p. 14·5°, b. p. 124—125°/14 mm., D^{15} 1·34.

Trichloromethyl chloroformate has b. p. 49°/50 mm. and 127°/750 mm., D^{15} 1·653. Its general properties resemble those of carbonyl chloride. On hydrolysis it gives carbon dioxide and hydrogen chloride, and with aniline water it yields *s*-diphenylcarbamide. With alcohols it gives the mixed trichloromethyl carbonates, and with sodium phenoxide yields *phenyl trichloromethyl carbonate*, m. p. 166°.

Anhydrous aluminium or ferric chloride decomposes it, giving carbon tetrachloride and carbon dioxide. W. G.

Determination of the Position of the Double Linking and its Transposition in some Unsaturated Compounds. (MLLE.) A. C. NOORDUYN (*Rec. trav. chim.*, 1919, **38**, 317—344).—The method adopted was to convert the unsaturated compound into its ozonide and decompose this by boiling it with water, the resulting aldehydes being, if necessary, oxidised to the acids for purposes of identification. By this method Goldsobel's formula for ricinoleic acid, $CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$ (compare A., 1895, 81), has been confirmed. Further evidence in support of this was obtained by the ozonisation of castor oil and subsequent decomposition of the ozonide. One of the products of this action, after oxidation, was the glyceride of azelaic acid,

$$C_3H_5(O\cdot CO\cdot[CH_2]_7\cdot CO_2H)_3,$$

D^{15} 1·0377, n 1·4693. Similarly, undecenoic acid was shown to have the formula $CH_2{:}CH\cdot[CH_2]_8\cdot CO_2H$, and one of the products of decomposition of its ozonide was the semi-aldehyde of sebacic acid, m. p. 126°, giving a *semicarbazone*, m. p. 168°.

Three unsaturated hydrocarbons, octylene, decylene, and heptadecylene, were prepared by the method of Grosjean (compare A., 1892, 691) by heating the barium salt of the next higher acid with sodium ethoxide, and it was shown by the ozonide method that the products, in every case, were mixtures of isomeric hydrocarbons. Similarly, the β-octylene of Kahlbaum, prepared by the action of zinc chloride on secondary octyl alcohol, was shown to be a mixture of isomerides.

By the fusion of oleic acid with potassium hydroxide there is formed not only acetic and palmitic acids, but a number of higher homologues of acetic acid and lower homologues of palmitic acid. Under similar conditions elaidic acid also gives a mixture of acids.

W. G.

Ghedda or East Indian Wax. II. Its Acids. A. LIPP and EUGEN KOVÁCS (*J. pr. Chem.*, 1919, [ii], **99**, 243—255. Compare A., 1912, i, 675).—The residue of potassium salts, after removal from the wax of alcohols and hydrocarbons in the manner previously described, furnished a mixture of acids, of which one was sparingly soluble in ether (see following abstract). From the remainder, after removal by steam of small amounts of formic and butyric acids, margaric acid and a previously unknown hydroxy-

margaric acid were separated by fractional extraction with light petroleum.

Hydroxymargaric acid, $C_{17}H_{34}O_3$, m. p. 58°, could not be distilled under reduced pressure. It was characterised as a normal acid by conversion into margaric acid through the action of hydriodic acid successively at 100° and at 200—220°. The intermediate iodomargaric acid was only obtained impure in the form of needles, m. p. 41·5°.
J. K.

Ghedda or East Indian Wax. III. Hydrocarbons and Acids. A. Lipp and E. Casimir (*J. pr. Chem.*, 1919, [ii], **99**, 256—258).—The wax contains approximately 48% of ceryl alcohol, 7% of hydrocarbons (5% of heptacosane, 2% of hentriacontane, with traces of a hydrocarbon of low melting point), 24—25% of hydroxymargaric acid, m. p. 55—56° (see preceding abstract), 1·5—2% of an isomeric hydroxymargaric acid, m. p. 71—72°, 9—10% of margaric acid, 8—9% of palmitic acid, 2% of "Ghedda" acid, and 1% of cerotic acid with traces of formic, acetic, and butyric acids and tarry matter. Cerotic and ghedda acids are present mainly in the free condition, the others in the form of their ceryl esters.

"*Ghedda*" *acid*, to which the formula $C_{34}H_{68}O_2$ is provisionally ascribed, m. p. 94·5—95°, forms mossy aggregates of white needles. Its sparing solubility in ether and that of its potassium salt in alcohol permit its separation from the other acids present. It differs from melissic acid, but is possibly identical with an acid obtained by Schalfeieff (this Journ., 1877, i, 454; compare, however, Nafzger, A., 1884, 1297).

Hydroxymargaric acid, $C_{17}H_{34}O_3$, m. p. 71—72°, forms needles or leaflets, and was isolated from the last light petroleum extracts of the mixed acids (see preceding abstract). Its *calcium* salt, $Ca(C_{17}H_{33}O_3)_2$, forms small, spherical nodules.

The hydrocarbon previously described (Lipp and Kuhn, A., 1912, i, 675) as $C_{30}H_{62}$, m. p. 70°, is now found to have m. p. 68—68·5°, and considered to be hentriacontane, $C_{31}H_{64}$, from its resemblance to the hydrocarbon obtained by Krafft from palmitone (A., 1882, 1272) and its identity with that prepared by Popp (*Diss.*, *Tech. Hochschule*, Munich, 1916), by reducing myricyl alcohol, which, on the other hand, he oxidised to melissic acid, at the same time establishing the formula $C_{31}H_{62}O_2$ for this acid (but see Heiduschka and Gareis, this vol., i, 134). Also the hydrocarbon, $C_{26}H_{54}$, m. p. 58°, is now found to have m. p. 59·5°, and considered to be heptacosane, $C_{27}H_{56}$, from its similarity to the hydrocarbon obtained from myristone by Krafft (*loc. cit.*).
J. K.

Crystallographic Investigation of the Dichlorosuccinic Acids. G. Aminoff (*Arkiv Kem. Min. Geol.*, 1917–18, **7**, No. 9, 1—11).—The optically active dichlorosuccinic acids have m. p. 166—167° and D^{15} 1·820. They are monoclinic-sphenoidal [$a:b:c = 2·3351:1:2·3754$, and $\beta = 101°30'$]. Twinning takes place along the plane $c\{001\}$, cleavage parallel with $x\{\bar{1}01\}$, and optical

extinction parallel to the edges [(100):(001)] and [(001):(011)]. The plane of the optical axis is parallel with *b*{010}.

The racemic acid has m. p. 174—175° and D^{15} 1·844. The crystals are monoclinic-prismatic, [*a*:*b*:*c*=0·5846:1:0·5994 and *β*=100°46′]. Cleavage takes place parallel to the axes *x*{101} and *b*{010}, and optical extinction parallel with the edges [(100):(001)] and [(001):(010)]. The optical axis is parallel with *b*{010}. It is not certain from the results whether the racemic acid is a true racemate.

*meso*Dichlorosuccinic acid has m. p. 217—218°. The crystals are monoclinic and needle-shaped, but they were not well enough developed to determine the crystallographic constants. T. S. P.

Apparatus for the Electrolytic Decomposition of Organic Acids at Low Temperature and with Small Volumes of Liquid. Electrolytic Decomposition of the Alkali Salts of Citraconic Acid. F. HENRICH and WILHELM SCHENK (*Ber.*, 1919, **52**, [*B*], 2120—2125).—The apparatus consists of a small flask, the bottom of which has been removed and the neck of which is provided with a cork holding a small inverted tube. The latter serves the two-fold function of diminishing the size of the apparatus to the required extent and of allowing efficient cooling by the introduction of a stream of cold water into the tube. As anode, a stout platinum wire or, preferably, a platinum gauze, is placed in close proximity to the tube. The cathode consists of a piece of nickel gauze. The apparatus is conveniently kept at a temperature of 25—40°. A gas-holder of the type previously recommended by Henrich (A., 1909, ii, 66) is used for collection of the anode gases and arrangements are also described which permit the analysis of these gases at any desired moment.

Electrolysis of concentrated, faintly alkaline solutions of potassium citraconate yields a mixture of oxygen, carbon dioxide, and allylene at the anode, the proportion of the latter increasing with increasing strength of current. Its production is also favoured by high concentration and low temperature, and is found to depend on the particular alkali salt used; the yields increase from lithium through sodium and potassium to rubidium, and then decline to cæsium. The authors consider that this behaviour supports the conception of Fichter and Krummenacher (A., 1918, i, 369) that electrolytic decomposition of organic acids is an oxidation process rather than the purely ionic hypothesis of Crum-Brown and Walker. H. W.

Electrolytic Decomposition of Glutaconic Acid. F. HENRICH and ADOLF HERZOG (*Ber.*, 1919, **52**, [*B*], 2126—2130).—The electrolytic decomposition of alkaline solutions of potassium glutaconate in the apparatus described in the preceding abstract leads to the formation of acetylene, acraldehyde, carbon monoxide, and carbon dioxide at the anode, these appearing to be the sole products of the action; the mechanism of the change has not been

fully elucidated, but the results appear to support the oxidation theory of electrolytic decomposition advanced by Fichter and Krummenacher (A., 1918, i, 369). H. W.

Glutaconic Acid. III. Condensation of Sodioformylacetic Ester with Cyanoacetic Ester. P. E. Verkade (*Vers. Akad. Wetensch. Amsterdam*, 1919, **27**, 1130—1139).—The product of reaction of these two substances is not ethyl α-cyanoglutaconate, as stated by other workers, but probably ethyl ωω′-dicyano-1:3-dimethyl*cyclo*butane-ω:ω′:2:4-tetracarboxylate.

Chemical Abstracts.

Preparation of Gluconic Acid. A. Herzfeld and G. Lenart (*Zeitsch. Ver. deut. Zuckerind.*, 1919, 122—128).—Kiliani and Kleemann's method (A., 1884, 993) has been modified in the following manner, so that the use of lead compounds for the elimination of the hydrobromic acid is obviated, the object in view being the elaboration of a technical process for the preparation of a substitute for vegetable acids. One part of dextrose (from starch), dissolved in 5 parts of water, is shaken in a closed vessel with 1 part of bromine until the disappearance of the latter. Oxidation is generally complete after twenty-four hours, at the end of which time the excess of bromine is distilled off in a vacuum, the temperature of the water-bath being about 50°. Heating is continued until the liquid commences to be coloured, when it is diluted with about 350 times its volume of water, and the hydrobromic acid neutralised by sodium carbonate. An excess of calcium carbonate is added gradually at a temperature of 90° (during which operation any lactone formed during distillation is transformed), and after two or three days the calcium salt separates out, and is recrystallised. By working up the mother liquors an almost quantitative yield may be obtained. If invert sugar is used in place of dextrose, the unchanged lævulose may be either precipitated as its insoluble calcium salt or converted into lævulic acid by boiling with dilute mineral acid. J. P. O.

The Hydrates of Heptaldehyde. (Mlle.) A. C. Noorduyn (*Rec. trav. chim.*, 1919, **38**, 345—350).—An examination of the system heptaldehyde–water shows the existence of a monohydrate and a dihydrate. No evidence of the existence of the hemihydrate described by Bussy (*Annalen*, 1846, **60**, 247) could be obtained.

W. G.

The Stabilisation of Acraldehyde. IV. Compounds Acting as Stabilisers against the Formation of Disacryl. Charles Moureu, Charles Dufraisse, and Paul Robin (*Compt. rend.*, 1919, **169**, 1068—1072. Compare A., 1919, i, 574; this vol., i, 10).—A study of the products present in the various fractions obtained by the fractional distillation of acraldehyde prepared by the dehydration of glycerol with potassium hydrogen sulphate shows that benzoic acid exerts a marked but variable stabilising action.

Phenol, found in some of the fractions, is also a stabilising age
but its activity is relatively feeble. W. G.

The Stabilisation of Acraldehyde. V. Stabilisi Action of Substances with a Phenolic Group. Charl Moureu, Charles Dufraisse, Paul Robin, and Jean Pougn (*Compt. rend.*, 1920, **170**, 26—31. Compare preceding abstract).—It has previously been shown that both phenol and benzoic ac exert a marked stabilising action against the formation of disac from acraldehyde. The study has now been extended to oth phenols and certain hydroxy-acids.

Of the monohydroxyphenols examined, α-naphthol shows t strongest stabilising action, and the presence of several hydro groups attached to ring carbon atoms causes a notable increase the stabilising power, except when two hydroxy-groups are in t meta-position to one another. The action of the various hydro benzoic acids is intermediate between that of the phenol and th of benzoic acid itself. Unlike the phenols, their methyl ethers their acetyl derivatives show little or no stabilising action. Si larly, the alcohols and the polyhydric alcohols do not exercise a stabilising action. Not only do the polyphenols inhibit the form tion of insoluble resin (disacryl) from acraldehyde, but they a exercise a similar inhibiting action against the formation of solu resin, even when the phenol is only present to the extent of 1 4000. W. G.

Oxidation of Mannitol by Nitrous Fumes. E. Votoč and C. Krauz (*Zeitsch. Zuckerind. Böhm.*, 1919, **43**, 577—580).—In the hope of finding a reagent which will effect the oxidation polyhydric alcohols to either aldehydic or ketonic substances exc sively, the authors have investigated the action of nitrous fumes an aqueous solution of mannitol; oxidation occurs slowly (but c be accelerated by the addition of a small quantity of a ferrous sa and leads to the formation of a mixture of mannose and lævulose H. W

Oximes of Rhodeose and Fucose. E. Votoček (*Zeits Zuckerind. Böhm.*, 1919, **43**, 572—574).—*Rhodeoseoxime*, m. 188—189°, is obtained in 97% yield by the action of Wol hydroxylamine solution on an aqueous solution of rhodeose; *fuc oxime* is similarly prepared, and has m. p. 188—189° when rapi heated. When treated with acetic anhydride and sodium aceta each oxime yields the same *acetylrhodeononitrile*, m. p. 177—17 whilst, in addition, a *substance*, m. p. 115—116°, which does appear to be an acetyl-nitrile, is obtained as by-product fr rhodeoseoxime. *iso*Rhodeose, in sharp contrast to rhamn rhodeose, and fucose, does not yield a sparingly soluble oxime. H. W

Action of Braun's Dihydrazine on certain Meth toses. E. Votoček (*Zeitsch. Zuckerind. Böhm.*, 1919, 577).—It has been shown by von Braun that diphe

this is possibly either an isomeride or a disulphide oxidation product of trithiodigalactose.

The isolation of a trithiodisaccharose affords an obvious explanation of the high sulphur content of the thio-sugars and their silver salts.

The contrast between the stability of the sulphur atom in thio*iso*trehalose (Schneider and Wrede, A., 1917, i, 540) and the instability of trithiodigalactose has led the authors to prepare thio- and seleno-digalactose, which are found to be perfectly stable substances; thus *octa-acetylthiodi*-d-*galactose*, colourless, slender needles, m. p. 200°, $[\alpha]_D^{18}$ −5·72 or −6·08°, in acetylene tetrachloride solution, is prepared by the interaction of bromoacetylgalactose on an alcoholic solution of potassium sulphide, and is transformed by methyl-alcoholic ammonia into *thiodi*-d-*galactose*, $C_{12}H_{22}O_{10}S$, colourless, pointed needles, m. p. 230°, $[\alpha]_D^{20}$ −41·86° in aqueous solution. The latter substance closely resembles thio*iso*trehalose in chemical properties; with mercuric chloride solution it yields a white precipitate, $2HgS,HgCl_2$. Similarly, *octa-acetylselenodigalactose* crystallises in small, colourless needles, m. p. 202°, $[\alpha]_D^{19}$ −13·4° or −12·5° in acetylene tetrachloride, and is converted by methyl-alcoholic ammonia into *selenodi*-d-*galactose*, slender needles grouped in clusters, m. p. 228°, $[\alpha]_D^{19}$ −36·6° or −37·6° in aqueous solution.

H. W.

Action of Hydrogen Sulphide on Sugars. II. WILHELM SCHNEIDER and OTTILIE STIEHLER (*Ber.*, 1919, **52**, [*B*], 2131—2135).—A further study of the action of hydrogen sulphide on dextrose and other sugars in pyridine solution (compare Schneider, A., 1916, i, 791).

The proportion of sulphur which enters the dextrose molecule is found to increase with the duration of the action and with increasing concentration of hydrogen sulphide, so that it appears that the system tends towards an equilibrium between unchanged and thio-sugar, water and hydrogen sulphide. Under suitable conditions, the dextrose molecule can combine with considerably more than one atom of sulphur.

Among the hexoses, *d*-galactose, *d*-mannose, and *d*-fructose react considerably more rapidly with hydrogen sulphide than does dextrose and absorb more than one atom of sulphur for each molecule; the behaviour of *l*-rhamnose and *l*-arabinose is similar. Lactose and maltose, on the other hand, only react very slowly, whilst α-methylglucoside and mannitol do not yield thio-compounds. The slight activity of penta-acetylglucose is probably due to the preliminary loss of one or more acetyl groups. The ability to yield thio-derivatives appears to depend on the presence of a reactive ketonic or aldehydic group in the molecule. H. W.

Action of Reducing Agents on the Chloraloses. M. HANRIOT and ANDRÉ KLING (*Ann. Chim.*, 1919, [ix], **12**, 129—150).—When the chloraloses are heated with ammonia in solution in perfectly dry methyl alcohol in sealed tubes at 150° for four to

six hours, one of the three atoms of chlorine is replaced by hydrogen, giving products which the authors name dechlorochloraloses. With benzoyl chloride these compounds give dibenzoyl derivatives. Thus β-chloralose gives *dechloro-β-chloralose*, $C_8H_{12}O_6Cl_2$, m. p. 156—157°, $[\alpha]_D$ −10·57°, giving a *dibenzoyl* derivative; α-chloralose gives *dechloro-α-chloralose*, m. p. 165°, $[\alpha]_D$ +9·96°, giving a *dibenzoyl* derivative, m. p. 146°. β-Galactochloralose gives the *compound*, $C_8H_{12}O_6Cl_2$, occurring in two forms, one having m. p. 96°, the other m. p. 133°; both have $[\alpha]_D$ −29·20°, and give a *dibenzoyl* derivative, m. p. 116°. β-Arabinochloralose gives the *compound* $C_7H_{10}O_5Cl_2$, m. p. 88—89°, $[\alpha]_D$ −19·72°, giving a *dibenzoyl* derivative, m. p. 90·5°.

On oxidation with nitric acid dechloro-β-chloralose gives a mixture of a lactone and an acid, from which, by the action of ammonia, *dechloro-β-chloralamide*, $C_7H_9O_5Cl_2\cdot CO\cdot NH_2$, m. p. 161—162°, is obtained. Under similar conditions dechloro-β-galactochloralose on oxidation only yields mucic acid. Dechloro-β-arabinochloralose yields an *acid*, $C_7H_8O_6Cl_2$, m. p. 215°.

When hydrolysed with hydrochloric acid the dechlorochloraloses simply split up, giving the sugar and dichloroacetaldehyde. The dechlorochloraloses may be more easily obtained, and with better yield, by the reduction of the corresponding chloralose with aluminium amalgam in neutral or acid aqueous alcoholic solution, or with a zinc–copper couple or zinc and sulphuric acid, or by electrolysis in acid solution. When reduced in alkaline solution, as by the action of sodium amalgam, the α- and β-chloraloses derived from dextrose each lose two atoms of chlorine, yielding respectively *bidechlorogluco-α-chloralose*, $C_8H_{13}O_6Cl$, m. p. 168°, giving a *dibenzoyl* derivative, m. p. 149°; and *bidechlorogluco-β-chloralose*, m. p. 166°, giving a *dibenzoyl* derivative, m. p. 146°. On oxidation, the former of these two compounds gave oxalic and saccharic acids, whilst the second gave a *lactone*, $C_7H_7O_5Cl$, isolated as its *hydrazone*, $C_7H_7O_5Cl,N_2H_4$, m. p. 170°.

Attempts to remove the third atom of chlorine from the chloraloses by reduction were not successful. W. G.

Catalytic Hydrogenation of Lactose. J. B. SENDERENS (*Compt. rend.*, 1920, **170**, 47—50).—A repetition of Ipatiev's work on the catalytic hydrogenation of lactose in aqueous alcoholic solution in the presence of nickel and nickel oxide (compare A., 1913, i, 10). It is now shown that if the catalyst is only slightly active, the reaction ceases when the aldehyde group is reduced to the group $\cdot CH_2\cdot OH$, and the author has isolated the resulting compound, which he calls *lactositol*,

$$OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot CH_2\cdot O\cdot \underbrace{CH\cdot[CH\cdot OH]_2\cdot CH}_{O}\cdot CH(OH)\cdot CH_2\cdot OH.$$

This compound has m. p. 78°, $[\alpha]_D$ +12·2°, and crystallises with $1H_2O$. On hydrolysis with dilute sulphuric acid it yields sorbitol and galactose.

If in the hydrogenation a more active catalyst is used, the action

proceeds further, the acetal group being attacked, hydrolysis occurs, and the resulting products are dulcitol and sorbitol. W. G.

Isolation of Inulin and Lævulose from Plant Sap. ARNOLD DANIEL (D.R.-P. 313986; from *Chem. Zentr.*, 1919, iv, 665).—The process depends on the addition of strongly alkaline substances in the warm, whereby the harmful non-inulin substances are partly precipitated and partly converted into a harmless form; the concentration of the alkali is to be so chosen that a further precipitation does not occur on treatment of the sap. The preparation of inulin from dahlia tubers by means of alkali hydroxides, or carbonates, or alkaline earths is described. Pure inulin may also be converted into pure lævulose and other degradation products of inulin, such as caramel and dextrin.

H. W.

Chemical Structure of the Lignin of Spruce Wood. PETER KLASON (*Arkiv Kem. Min. Geol.*, 1917, **6**, No. 15, 1—21). —Spruce wood has previously been shown to consist approximately of: 50% cellulose, 16% other carbohydrates, 30% lignin, and 4% of other substances. Since the "other carbohydrates" have become of great practical importance, the name "lignosans" is suggested for them.

The composition of lignin has previously been derived from a study of barium lignosulphonate and found to be $C_{40}H_{40}O_{11}$ (compare A., 1908, i, 717, the composition then being wrongly given as $C_{40}H_{42}O_{11}$). *Calcium lignosulphonate*, $C_{40}H_{44}O_{18}S_2Ca$, has now been prepared; it apparently contains one molecule more water than the barium salt, and gives a cryoscopic molecular weight of 1628—1753, so that it forms double molecules in aqueous solution. Lignin would then have the composition

$$C_{40}H_{44}O_{18}S_2Ca-Ca(HSO_3)_2 = C_{40}H_{42}O_{12},$$

that is, it results from the condensation of 1 mol. of coniferyl alcohol and 3 mols. of hydroxyconiferyl alcohol with the loss of 3 mols. of water. (This composition is apparently taken as preferable to that obtained from the barium salt.) *Naphthylamine lignosulphonate* is readily obtained as a yellow, sandy powder by precipitating a solution of the calcium salt with naphthylamine hydrochloride.

When the mother liquors, from which the above calcium salt has been precipitated, are heated with naphthylamine hydrochloride, a *naphthylamine lignosulphonate*, $C_{59}H_{60}O_{14}S_2N_3$, different from the above, is precipitated. This can be considered as made up of: 1 mol. of coniferyl alcohol, 1 mol. of hydroxyconiferyl alcohol, 1 mol. of caffeic acid, 2 mols. of H_2SO_3, and 3 mols. of naphthylamine, the condensation of the first three components taking place with the loss of 3 molecules of water. The lignin forming the basis of this salt would thus have the formula $C_{29}H_{26}O_8$, and contain two methoxy-groups. Assuming that the lignin of wood is made up of an equal number of molecules of the two above lignins, its formula would be $C_{69}H_{68}O_{20}$, with six methoxy-groups, and such a composition agrees very well with analytical data.

It is suggested that the condensations above mentioned take place between the hydroxyl of an allyl alcohol group and the phenolic hydroxyl in another molecule, and so on, lignin thus being built up on the same principle that holds for polysaccharides and albumins.

The reason for including caffeic acid in the building up of the *lignin* $C_{29}H_{26}O_8$ *is that an acid residue must be present to account* for the third molecule of naphthylamine in the salt, the other two molecules being bound by the sulphurous acid. Plant products are often substituted benzene derivatives, the first position being occupied by allyl alcohol or acrylic acid residues, whilst the positions 3, 4, and 5 are occupied by hydroxyl or methoxyl groups; caffeic acid is such a derivative.

The results obtained by the dry distillation of wood are in agreement with the above deductions, and all known facts agree with the assumption that lignin from spruce wood results from the condensation of methylated hydroxycinnamyl alcohols or the corresponding aldehydes and acids, which are substituted similarly to protocatechuic acid.

Combinations of lignin and sulphite have the character of tannins, and lignin can be considered to be an insoluble tannin.

Investigation of the molecular weight of the above-mentioned calcium lignosulphonate by the ebullioscopic method gives the value 982 (theory, 916), so that at the boiling point it is not associated; the potassium salt gave similar results. Lignin prepared from spruce wood by digesting it with alcoholic sulphuric acid and removing the fat and resin with light petroleum gave a molecular weight of 650 in glacial acetic acid, as compared with the theoretical value 714 for $C_{40}H_{42}O_{12}$, that is, in agreement with the formula for the lignosulphonate.

Experiments on the behaviour of coniferin and coniferyl alcohol towards acid sulphites gave results in agreement with the assumption that lignin contains aromatic nuclei of the same structure as coniferyl alcohol, together with side-chains of the same constitution as allyl alcohol. The lignin reactions (compare A., 1908, i, 717), which are also given by calcium lignosulphonate after treatment with alkali, point to the same conclusion.

The final conclusion of the author is that lignin in wood is built up from pentoses, as the following equation, which gives dihydroxycinnamyl alcohol, indicates: $2C_5H_{10}O_5 = C_9H_{10}O_3 + 5H_2O + CO_2$. The methylation of the phenolic groups may be brought about by formaldehyde, $R{\cdot}OH + CH_2O = R{\cdot}OCH_3 + O$, the oxygen liberated then changing RH into R·OH, and also oxidising allyl alcohol complexes into the corresponding aldehydes and acids, thus giving the complexes shown to be present in lignin. T. S. P.

Preparation of Hexamethylenetetramine Dinitrate. ZENTRALSTELLE FÜR WISSENSCHAFTLICH-TECHNISCHE UNTERSUCHUNGEN (D.R.-P. 298412; from *Chem. Zentr.*, 1919, iv, 498—499).—Solid hexamethylenetetramine is added, preferably with cooling, to

dilute aqueous nitric acid, which may contain sulphuric acid Separation of the *salt* occurs so completely (about 95% of that theo retically possible) that the reaction may be applied immediately t the precipitation of nitric acid from its aqueous solution. H. W.

Reduction of Methylene-blue by Glycine. FRIEDRICH HASSE (*Biochem. Zeitsch.*, 1919, **98**, 159—177).—Glycine reduce methylene blue in alkaline solution. Other amino-acids do not give this reaction. Quantitative estimations show that acetaldehyde and dextrose give a weaker, creatine, catechol, and resorcinol an equal and glucosamine and to a much greater extent adrenaline and quinol a higher reduction than glycine. These observations are discussed in relation to the Strecker-Traube reactions.

S. S. Z.

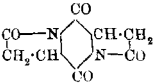
Calcium Haloid Salts of Carbamide and Asparagine YUZURU OKUDA and KIYOSHI FUJIWARA (*J. Tokyo Chem. Soc.* 1919, **40**, 404—412).—Carbamide and asparagine form double compounds with calcium haloids, which are easily crystallised. Thus the *compound*, $CaI_2,6CO(NH_2)_2$, m. p. 168—169°, hexagonal plates having a bitter taste, is obtained by passing hydrogen sulphide into a mixture of powdered calcium carbonate, iodine, and a little water until the iodine has dissolved, removing the excess of carbonate and adding carbamide to the filtrate, which is then made slightly alkaline with lime-water; the crystals are obtained by concentrating the solution, and are recrystallised from water or alcohol. Other compounds described are: $CaBr_2,6CO(NH_2)_2$, m. p. 146°, hexagonal plates; $CaCl_2,4CO(NH_2)_2$, hygroscopic, hexagonal crystals $CaI_2,C_4H_8O_3N_2,4H_2O$, m. p. 136°; $CaBr_2,C_4H_8O_3N_2,4H_2O$; and $CaCl_2,C_4H_8O_3N_2,4H_2O$, m. p. 67°, hygroscopic, columnar crystals.

CHEMICAL ABSTRACTS.

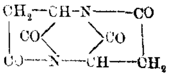
Transformation of Asparagine into the Dipeptide of Aspartic Acid. C. RAVENNA and G. BOSINELLI (*Atti R. Accad Lincei*, 1919, [v], **28**, ii, 113—117).—When ordinary *l*-asparagine is subjected to prolonged boiling in aqueous solution, it undergoes partial racemisation (compare Pringsheim, A., 1910, i, 303; ii, 437) From the inactive asparagine separable from the solution by crystallisation, the *d*-isomeride may be obtained pure by dissolving a little magnesium sulphate and potassium and calcium hydrogen phosphates in the 2% aqueous solution and leaving the latter exposed for fifteen days to the air at the ordinary temperature; the mould which develops on the liquid rapidly attacks the *l*-asparagine, and the *d*-asparagine may afterwards be crystallised out.

The mother liquors from the inactive asparagine yield no further crystals, but are found to contain the dipeptide of aspartic acid (asparagylaspartic acid) (compare Fischer and Koenigs, A., 1907, i, 486), $CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$. The latter may be purified by heating it in an open vessel for some hours

at 210°, this treatment converting it into diketopiperazinediacetic anhydride,



or, more probably,



which neither melts nor decomposes at 320°; by baryta water in the cold this anhydride is transformed into asparagylaspartic acid.

In view of the widespread occurrence of asparagine in plants and the importance of the polypeptides in relation to the synthesis of proteins, it seems possible that the ready formation of the dipeptide of aspartic acid from asparagine may play a part in vegetable metabolism. T. H. P.

Transformation of Ammonium Malate into the Dipeptide of Aspartic Acid. C. RAVENNA and G. BOSINELLI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 137—139).—The composition and characters of diketopiperazinediacetic anhydride (compare preceding abstract) indicate the identity of this compound with that obtained by Dessaignes (Beilstein, 3rd edition, I, 1389) by heating ammonium hydrogen malate, and described in the older literature as fumarimide. The conversion of the latter compound into the dipeptide of aspartic acid by the action of baryta solution in the cold confirms the identity. T. H. P.

Chloroacetates of *S*-Alkylthiocarbamides. JOHN TAYLOR (T., 1920, **117**, 4—11).

Equilibrium Conditions in the Bucher Process for the Fixation of Nitrogen. J. H. FERGUSON and P. D. V. MANNING (*J. Ind. Eng. Chem.*, 1919, **11**, 946—950).—In Bucher's process for the fixation of nitrogen the main reaction is represented by the equation $2Na_2CO_3 + 4C + N_2 \rightleftharpoons 2NaCN + 3CO$, the iron apparently acting only as catalyst. In order to ascertain the empirical relationships which may be taken as representing the probable conditions of equilibrium in practice, a stream of gas of varying composition was passed over the charge, which was heated in an iron boat and the amounts of carbonate converted into cyanide at the equilibrium points were estimated. It was found that the iron boat was not affected in experiments at 950° to 1000° in which the gas contained up to 80% of carbon monoxide. Curves were plotted showing the percentage formation of cyanide in relation to the proportion of carbon monoxide in the initial gas. The results indicated that the temperature has relatively little influence on the conversion when the gas contains little carbon monoxide, but would have much more influence in the case of gas, such as producer gas, containing, say, 30% of carbon monoxide. At 1000° it is possible to convert up to about 60% of the alkali carbonate by means of pro-

ducer gas, and the yield would be increased by the use of a higher temperature. The amount of conversion decreases with the rise in the proportion of carbon monoxide in the initial gas, and in the case of gas containing 60% of carbon monoxide only half of the carbonate is converted. The results also indicated that the initial reduction of the sodium carbonate to sodium is the controlling factor in the Bucher process, and that the effect of the carbon at this stage may be to maintain the pressure of the carbon dioxide below that of the dissociation pressure of the carbonate. This view received support from the results obtained by plotting the amounts of carbonate converted into cyanide in relation to carbon dioxide instead of carbon monoxide. [See, also, *J. Soc. Chem. Ind.*, 1920, **17A**.]

C. A. M.

Action of Mercuric Cyanide on Metallic Salts. LILANANDA GUPTA (T., 1920, **117**, 67—73).

Effect of Pressure, and of Dissolved Air and Water on the Melting Point of Benzene. THEODORE W. RICHARDS, EMMETT K. CARVER, and WALTER C. SCHUMB (*J. Amer. Chem. Soc.*, 1919, **41**, 2019—2028).—The freezing point of benzene and the effect of dissolved air and water on this quantity have been experimentally investigated. It is shown that benzene saturated with air under atmospheric pressure melts 0·003° below the true triple point. Benzene thus saturated has its freezing point but little altered by change of pressure. There appears to be no large amount of supersaturation. The effect of pressure in the absence of dissolved air is shown to alter the freezing point 0·029° per atmosphere. Saturation with water lowers the freezing point of benzene 0·095°. The true freezing point of benzene saturated with air is probably not far from 5·493° and the true triple point not far from 5·496°.

J. F. S.

The Nitrotoluenes. III. Binary Systems of the Components: *p*-Nitrotoluene, 2:4-Dinitrotoluene, and 2:4:6-Trinitrotoluene. JAMES M. BELL and CHARLES H. HERTY, Jun. (*J. Ind. Eng. Chem.*, 1919, **11**, 1124—1128. Compare this vol., i, 22, 23).—The melting points of two-component systems of three of the principal nitration products of toluene have been determined by the cooling-curve method, and the complete results plotted in curves. The term "melting point" is defined as the temperature at which crystals first appear, and in determining it the question of super-cooling has to be taken into consideration, whilst the eutectic point is the temperature at which there is equilibrium between the solids and melted mass. The probable values found for the melting points were: For *p*-nitrotoluene (*MNT*), 51·5°; 2:4-dinitrotoluene (*DNT*), 69·6°; and 2:4:6-trinitrotoluene (*TNT*), 80·35°, in each case with a + or − error of 0·3°. In the binary system *MNT*–*TNT* the eutectic points were 33·85—33·95°; in the system *DNT*–*TNT*, 45·4—45·6°; and in the system *MNT*–*DNT*, 26·44—26·54°. In no instance did the freez-

ing-point curves intersect at other than the eutectic temperature points, and the conclusions of Giua (A., 1914, i, 817) as to the existence of molecular compounds in these three cases were therefore not supported by these results. C. A. M.

The Nitrotoluenes. IV. The Three-component System: *p*-Nitrotoluene, 2 : 4-Dinitrotoluene, and 2 : 4 : 6-Trinitrotoluene. JAMES M. BELL and CHARLES H. HERTY, Jun. (*J. Ind. Eng. Chem.*, 1919, **11**, 1128—1130).—The freezing points of mixtures of these compounds have been determined and plotted in the conventional triangular diagrams, the primary freezing point being the temperature at which the first solid separated, the second that at which the second solid separated, and the eutectic point that at which all three solids were in equilibrium with the melted mass. The diagram thus consisted of three fields separated by three boundary curves, which intersected at the ternary eutectic point. No evidence was obtained pointing to the existence of binary molecular compounds as claimed by Giua (see preceding abstract). By a method of interpolation both the composition and temperature of points on the boundary curves may be found, and in this way it is possible to identify the composition of a mixture of the three compounds from the determination of the freezing points. C. A. M.

***p*-Cymene. III. Preparation of 2-Chloro-5 : 6-dinitro-*p*-cymene.** H. A. LUBS and R. C. YOUNG (*J. Ind. Eng. Chem.*, 1919, **11**, 1130—1133. Compare A., 1918, i, 339; 1919, i, 398).—The chief product formed in the nitration of 2-chloro-*p*-cymene is 2-chloro-5 : 6-dinitro-*p*-cymene, whilst an isomeric compound also appears to be formed. Another chlorodinitro-compound (m. p. 90—91°) containing less carbon than chlorodinitrocymene is also formed in small quantity, together with a substance of unknown composition, possibly a chloroterephthalic acid. C. A. M.

4-Chlorobenzene-1 : 3-disulphonic Acid and its Transformation into the Symmetrical Compound. S. C. J. OLIVIER (*Rec. trav. chim.*, 1919, **38**, 351—355).—4-Chlorobenzene-1 : 3-disulphonic acid gives a *potassium* salt, $C_6H_3Cl(SO_3K)_2,H_2O$, a *barium* salt, $C_6H_3Cl(SO_3)_2Ba,4H_2O$, and a *dichloride*,

$$C_6H_3Cl(SO_2Cl)_2,$$

m. p. 90·5°.

When the anhydrous barium salt is heated with sulphuric acid, containing some sulphur trioxide, at 300° for five hours it is partly converted into *5-chlorobenzene-1 : 3-disulphonic acid.* W. G.

The Structure of the Chlorobenzenedisulphonic Acid prepared according to D.R.-P. 260563. S. C. J. OLIVIER (*Rec. trav. chim.*, 1919, **38**, 356—357).—By preparation and identification of its acid chloride it is shown that the acid obtained by the sulphonation of *p*-chlorobenzenesulphonyl chloride by the method of Meister, Lucius, and Brüning (D.R.-P. 260563) is 4-chlorobenzene-1 : 3-disulphonic acid. W. G.

Iodination of Aromatic Amines by means of Iodine and Persulphate. K. Elbs and H. Volk (*J. pr. Chem.*, 1919, [ii], **99**, 269—275. Compare A., 1913, i, 841).—The success of this method when applied to aromatic amines and their acyl derivatives is very limited. The yields of 2-iodo-*p*-nitroaniline (*acetyl* derivative, needles, m. p. 128—130°) and 2:4-di-iodo-*o*-nitroaniline were good; of 2-iodo-*p*-toluidine and 2-iodosulphanilic acid, moderate; of 2:4-di-iodoaniline (accompanied by *p*-iodoaniline), *p*-iodoacetanilide, and 3-iodo-*p*-bromoaniline, poor. Indefinite products were obtained from *m*-xylidine, dimethylaniline, diphenylamine and its acetyl derivative, *p*-chloroaniline, *m*-bromoaniline, and *m*-nitroaniline, as well as from anisidine and phenacetin, although unpublished experiments with anisole and phenetole had given excellent results. Tribenzylamine was oxidised to benzaldehyde, and hexamethylenetetramine gave its additive di-iodide.

Except in the case of acetanilide, the acetic acid used in the earlier experiments was replaced by concentrated hydrochloric acid.

J. K.

A New Modification of 3:4-Dinitromethylaniline. Herbert Swann (T., 1920, **117**, 1—4).

Acylvanillylamides. E. K. Nelson (*J. Amer. Chem. Soc.*, 1919, **41**, 2121—2130).—Having shown capsaicin to be decenovanillylamide (compare A., 1919, i, 543), the author has prepared a number of acylvanillylamides and approximately determined their pungency. These amides are readily prepared by action on vanillylamine with the requisite acyl chloride. *Acetovanillylamide* has m. p. 84—85° (corr.); n_α 1·550; n_β 1·585; n_γ 1·685; *propiovanillylamide* has m. p. 108—110° (corr.); n_α 1·495; n_β 1·635; n_γ 1·680; n-*butyrovanillylamide* has m. p. 68—70° (corr.); n_α 1·515; n_β 1·580; n_γ 1·655; iso*butyrovanillylamide* has m. p. 118—120°; n_α 1·465; n_β 1·633; n_γ 1·635; n-*hexovanillylamide* could not be obtained crystalline; n-*heptovanillylamide* has m. p. 59—61° (corr.); n_α 1·515; n_β 1·595; n_γ 1·625; n-*octovanillylamide* has m. p. 41—43° (corr.); n_α 1·56; n_γ 1·57; n-*nonovanillylamide* has m. p. 52°; n_α 1·57; n_γ 1·59; n-*decovanillylamide* has m. p. 59—60°; n_α 1·545; n_β 1·555; n_γ 1·620; n-*undecovanillylamide* has m. p. 54—56°; n_α 1·515; n_β 1·540; n_γ 1·615; n-*dodecovanillylamide* has m. p. 60—61° (corr.); n_α 1·52; n_β 1·540; n_γ 1·60; *crotonovanillylamide* has m. p. 119—120° (corr.); n_α 1·515; n_β 1·605; n_γ 1·735; *undecenovanillylamide* has m. p. 53—55° (corr.); n_α 1·55; n_β 1·60; n_γ 1·63; *benzovanillylamide* has m. p. 140—142°; n_α 1·590; n_β 1·675; n_γ 1·695.

Below the *n*-hexoamide these substances have little or no pungency, but above this member the pungency increases rapidly with rise in molecular weight to the nonoamide and then diminishes again.

W. G.

***N*-Methylvinylaniline.** Julius von Braun and Georg Kirschbaum (*Ber.*, 1919, **52**, [*B*], 2261—2265).—The substance is mainly of interest because it represents the first amine to be investi-

gated which contains the vinyl group directly united to the nitrogen atom.

Methyl-β-bromoethylaniline is converted by trimethylamine into the quaternary bromide, $NMePh\cdot CH_2\cdot CH_2\cdot NMe_3Br$, the bromine atom of which is not removed by protracted boiling with 51% potassium hydroxide solution; the corresponding quaternary base may, however, be obtained by the action of silver oxide, and, when heated under diminished pressure, yields *methylvinylaniline*; the success of the operation is dependent on the purity of the bromide. The freshly distilled base forms a colourless liquid with a sharp *odour resembling that of formaldehyde or acetaldehyde. It has* $D_4^{17.95}$ 0·9887. It differs from other anilines and bases in its instability and susceptibility to change; when preserved, even with exclusion of light, it gradually becomes more viscous; after 48 hours it has $D_4^{17.7}$ 1·0144, after 96 hours $D_4^{17.3}$ 1·0408, whilst after 144 hours it is too viscous to allow determination of density. When distilled, it boils mainly at 98—99°/16 mm., but about one-third of the base is converted into a dark red, viscous mass, probably by the alkali of the glass. A further remarkable property is the ease with which the vinyl group is removed in the form of acetaldehyde by hydrolysing agents, the reaction occurring even with boiling water. For this reason, it has not been found possible to isolate pure salts or derivatives of the base.

The properties of methylvinylaniline throw doubt on the probability of the presence of the vinyl group attached to nitrogen in morphine, as has been postulated by Wieland and Kappelmeier.

H. W.

The Nitro-derivatives of Diphenylamine. M. C. F. van Duin and B. C. Roeters van Lennep (*Rec. trav. chim.*, 1919, **38**, 358—368).—An endeavour to determine the position of the last two nitro-groups in 2 : 4 : 6 : 3′ : ? : ?-hexanitrodiphenylamine, formed by nitrating 2:4:6:3′-tetranitrodiphenylamine in the cold (compare Austen, this Journ., 1875, 165).

2:4:6:2′:4′-Pentanitrodiphenylamine, m. p. 196—197° (corr.), is easily prepared by saturating nitric acid (D 1·49) with picrylaniline at a temperature not exceeding 25°.

2:4:6:2′:4′:6′-Hexanitrodiphenylamine may be prepared by nitrating picrylaniline in a nitric–sulphuric acid mixture or by nitrating pentanitrodiphenylamine at 70°. It has m. p. 249° (decomp.).

2:4:6:2′(?):3′:4′-Hexanitrodiphenylamine, m. p. 273—274°, is obtained by nitrating the 2:4:6:3′-tetranitro-compound in a nitric–sulphuric acid mixture at the ordinary temperature. The nitro-group in the position 3′ is very mobile; ammonia and the amines react immediately with it at the ordinary temperature. Thus dimethylamine gives *pentanitrodimethylaminodiphenylamine*, m. p. 249° (corr.).

2:4:6:3′:4′-*Pentanitrodiphenylamine*, m. p. 232° (corr.), may be prepared by heating together picryl chloride and 3:4-dinitroaniline in a sealed tube at 140° for eight hours, and this may be

converted into the hexanitro-derivative, m. p. 273—274°, given above, thus establishing the position of the nitro-group at 4′.

In an endeavour to establish the position of the sixth nitro-group, 3 : 4 : 6 trinitrodimethylaniline was heated in alcoholic solution with aniline in a sealed tube at 120°, the product being 4 : 6-*dinitro-3-anilinodimethylaniline*, m. p. 143° (corr.). This was then nitrated, but, instead of the required pentanitrodimethylaminodiphenylamine, as described above, being obtained, the product was 2 : 4 : 6 : 2′ : 4′-*pentanitro-5-methylnitroaminodiphenylamine*, m. p. 224—225° (corr.), which may also be prepared from 3-anilino-2 : 4 : 6 trinitrophenylmethylnitroamine, the intermediate product being 2 : 4 : 6 : 2′-*tetranitro-5-methylnitroaminodiphenylamine*, m. p. 200° (corr.).

By the action of *p*-nitroaniline on tetranitrophenylmethylnitroamine in boiling benzene solution, there is obtained a mixture of a *compound*, m. p. 235° (corr.), and 2 : 4 : 6 : 4′-*tetranitro-5-methylnitroaminodiphenylamine*, m. p. 200°. W. G.

History of the Discovery of Oxonium Salts from Phenol Ethers. F. Kehrmann (*Ber.*, 1919, **52**, [*B*], 2119).—The recent publication of Meyer and Gottlieb-Billroth (this vol., i, 37) on the action of nitric acid on phenol ethers leads the author to point out that the oxonium compound from thymol ethyl ether has been studied by Kehrmann and Messenger (*Ber.*, 1901, **34**, 1626), and its constitution has been elucidated by Decker and Solonina (A., *1902, i, 767*). H. W.

Preparation of *p*-Phenetolecarbamide. J. D. Riedel (D.R.-P. 313965; from *Chem. Zentr.*, 1919, iv, 738).—Solutions of alkali cyanides are treated successively with alkaline oxidising agents and phenetidine hydrochloride; *p*-phenetolecarbamide separates immediately in good yield and in a highly pure condition. Sodium hypochlorite or sodium peroxide is cited as oxidising agent. H. W.

Preparation of Acyl Derivatives of Cholic Acid. J. D. Riedel (D.R.-P. 313413; from *Chem. Zentr.*, 1919, iv, 738—739). —*o*-Acetoxybenzoyl chloride is allowed to react with cholic acid in the presence of a substance which will combine with halogen acid. The *product* obtained from these substances in the presence of pyridine is a colourless, crystalline powder, insoluble in water, soluble in alcohol, m. p. 120°; it is tasteless and does not cause digestive disorders. It appears to be unchanged in the stomach, but to be readily dissolved in the intestines. It combines the pharmacological action of cholic and salicylic acids, and is expected to find application in pharmacy. H. W.

Molecular Rearrangement in the Acylation of certain Aminophenols. L. Chas. Raiford (*J. Amer. Chem. Soc.*, 1919, **41**, 2068—2080).—5-Bromo-3-amino-*p*-cresol, when acetylated, yielded 5-*bromo-3-acetylamino*-p-*tolyl acetate*, m. p. 169°, which, when hydrolysed, gave 5-*bromo-3-acetylamino*-p-*cresol*, m. p. 129°.

This compound, when benzoylated, yielded 5-*bromo-3-benzoylamino*-p-*tolyl acetate*, m. p. 172°, molecular rearrangement thus occurring The constitution of the latter compound was proved by hydrolysing it, when 5-*bromo-3-benzoylamino*-p-*cresol*, m. p. 185°, was obtained identical with that prepared by benzoylating 5-bromo-3-amino-*p*-cresol by using 1 mol. of benzoyl chloride in ethereal solution with 2 mols. of the aminophenol.

A similar series of compounds was prepared from 4 : 6-dibromo-2-aminophenol. On acetylation, it yielded 4 : 6-*dibromo-2-acetylaminophenylacetate*, m. p. 199°, which, when treated with aqueous sodium hydroxide, gave 4 : 6-*dibromo-2-acetylaminophenol*, m. p. 174—175° (decomp.), and this with benzoyl chloride gave 4 : 6-*dibromo-2-benzoylaminophenyl acetate*, m. p. 195—196°. This acetate, on saponification, gave 4 : 6-*dibromo-2-benzoylaminophenol*, m. p. 198°, identical with that obtained by benzoylating 4 : 6-dibromo-2-aminophenol in dry ether.

In both these cases, therefore, the diacyl derivative always had the heavier benzoyl radicle attached to nitrogen, regardless of the order in which the radicles were introduced. As this is in direct opposition to the results obtained by Ransom and Nelson (compare A., 1914, i, 269), similar experiments were conducted with aminophenol itself, and, regardless of the order of introduction of the acyl radicles, the final product was 2-*benzoylaminophenyl acetate*, m. p. 135°. Thus in these cases no differences have been observed between the behaviour, in this respect, of substituted and unsubstituted aminophenols, which indicates that acid-forming substituents are not responsible for the rearrangement. W. G.

Halogenation. XIX. The Replacement of Sulphonic Groups by Chlorine and the Preparation of Organic Chloro-derivatives. RASIK LAL DATTA and HARAPARBUTTY KUMAR MITTER (*J. Amer. Chem. Soc.*, 1919, **41**, 2028—2038).—When chlorine is passed into an aqueous solution of a sulphonic acid, the sulphonic group is readily replaced by chlorine, with very good yields. In some cases, additional chlorination also takes place. Aromatic substances which, in addition, contain an hydroxy-group exhibit a special facility for this displacement of the sulphonic group by chlorine, and the same has also been found true of amino-compounds, such as the nitroanilines. Under these conditions, anisole- and phenetole-sulphonic acids yield tetrachloroketo*cyclo*hexadiene and some trichlorophenol. Phenolsulphonic acid gives trichlorophenol; *o*-cresol-5-sulphonic acid gives 5-chloro-*o*-cresol; *m*-cresol-6-sulphonic acid and *m*-cresol-2 : 6-disulphonic acid both give 2 : 6-dichloro-*m*-cresol; *p*-cresol-3-sulphonic acid gives a *trichloro*-p-*cresol*, m. p. 85—86°, which is either the 2 : 3 : 6- or the 2 : 5 : 6-trichloro-derivative; *p*-cresol-3 : 5-disulphonic acid gives 3 : 5-dichloro-*p*-cresol. Thymol mono- and di-sulphonic acids both give 2 : 5 : 6-trichlorothymol; carvacrol-5-sulphonic acid gives trichlorocarvacrol; orcinoldisulphonic acid gives pentachloro-orcinol [3 : 5-diketomethylpentachloro*cyclo*hexane]. *o*- and *p*-Nitrophenolsulphonic acids give, respectively, 4 : 6-dichloro-*o*-nitrophenol and

2:6-dichloro-*p*-nitrophenol; *o*- and *p*-nitroanilinesulphonic acid yield, respectively, 4:6-dichloro-*o*-nitroaniline and 2:6-dichloro-*p*-nitroaniline, whereas *m*-nitroanilinesulphonic acid does not give an definite product. Salicylic acid, on sulphonation and subsequen chlorination, gives 3:5-dichlorosalicylic acid. 2:4:6-Trisulpho-*m*-hydroxybenzoic acid gives the corresponding trichloro-derivative and 3-sulpho-*p*-hydroxybenzoic acid yields 3:5-dichloro-*p*-hydroxybenzoic acid. W. G.

Replacement of Sulphonic Groups by Nitro-groups by means of Nitrous Gases. Rasik Lal Datta and Phuldeo Sahaya Varma (*J. Amer. Chem. Soc.*, 1919, **41**, 2039—2048).—The sulphonic acid group in aromatic compounds may be very easily replaced by nitro-group by means of nitrous gases. The action is generally effected in aqueou solutions, the nitrous gases being passed until saturation is reached. In the course of the action more nitro-groups frequently enter with the formation of highly nitrated compounds. Many nitration which cannot be brought about at all by nitric acid can be smoothl accomplished by this method. The reaction may be used for determining the constitution of nitro-compounds derived from know sulphonic acids. Aromatic compounds which are already substituted by hydroxy-groups or by halogens readily undergo replacement o the sulphonyl group by a nitro-group, in some cases more nitro groups entering the ring in suitable positions. In the case o hydroxycarboxylic acids containing a sulphonyl group, both th sulphonyl and the carboxyl groups are replaced by nitro-groups. If, however, the compound does not already contain substituen halogens or hydroxyl groups, replacement of the sulphonyl grou does not take place at all. Thus benzenesulphonic acid remain unacted on by treatment with nitrous gases.

By this method the following compounds have been prepared 3:4-Dinitro-*o*-cresol from either *o*-cresol-3-sulphonic acid or *o*-creso 4-sulphonic acid; 3:5-dinitro-*o*-cresol from the 3:5-disulphonic acid 2:4:6-trinitro-*m*-cresol from either *m*-cresol-6-sulphonic acid or th 2:6-disulphonic acid; 3:5-dinitro-*p*-cresol from *p*-cresol-3-sulphoni acid; 3:5-dinitro-*o*-4-xylenol from *o*-xylenol-4-sulphonic acid 5-nitro-*m*-4-xylenol and 2-nitro-*p*-5-xylenol from the correspondin sulphonic acids; 6-nitrothymol from thymolsulphonic acid; 2:4:6-trinitroresorcinol from either resorcinoldisulphonic acid, *m*-nitrophenolsulphonic acid, or *m*-hydroxysulphobenzoic acid; 2:4-dinitrophenol from either anisole- or phenetole-sulphonic acid; 2:4:6-trinitrophenol from the sulphonic acids of either *o*- or *p*-nitrophenol or *o*- or *p*-hydroxybenzoic acid. By direct sulphonation and subsequent treatment with nitrous gases without isolation of the sulphonic acid, 1:2:3-cresotic acid gave 3:5-dinitro-*o*-cresol; 1:3:4-cresotic acid gave 2:4:6-trinitro-*m*-cresol; 1:4:3-cresotic aci gave 3:5-dinitro-*p*-cresol; chloro-, bromo-, and iodo-benzenes gav the corresponding *p*-nitro-derivatives; phenylacetonitrile gav *p*-nitrophenylacetonitrile; and anthraquinone gave β-nitroanthraquinone. W. G.

Preparation of Tetrahydro-β-naphthol. GEORG SCHROETER and WALTER SCHRAUTH (D.R.-P. 299603; *from Chem. Zentr.*, 1919, iv, 618).—Tetrahydronaphthalene-β-sulphonic acid or its salts are fused with alkali. The acid is prepared by mixing tetrahydronaphthalene with a small excess of concentrated or absolute sulphuric acid; in the latter case the hydrocarbon dissolves immediately with spontaneous warming of the solution to 80—100°, and the process is completed by warming the mixture on the water-bath. On cooling, the mixture solidifies to a mass of crystals, from which the sulphonic acid can be isolated by pressure; alternatively, the alkali salts may be obtained by neutralising the slightly diluted mixture with alkali hydroxide and cooling, or may be salted out with potassium or sodium chloride. In addition, the alkali salts are prepared by the hydrolysis of tetrahydronaphthalene-β-sulphonyl chloride (from the hydrocarbon and chlorosulphonic acid). When fused with potassium or sodium hydroxide, either singly or together or with addition of milk of lime, tetrahydronaphthalene-β-sulphonic acid or its alkali salts are smoothly transformed, at 230—300°, into *tetrahydro-β-naphthol*, silky needles, m. p. 59—60°, b. p. 145—146°/13 mm., 275—276°/760 mm., which is readily soluble in alkali hydroxide, in solutions of salts of the fatty and sulpho-fatty acids, and in concentrated sulphuric acid. The soap solutions remain permanently clear when diluted with conductivity water, whilst the naphthol is again precipitated when the sulphuric acid solutions are diluted. When the sulphuric acid solution is warmed, *tetrahydro-β-naphthol-α-sulphonic acid* is formed, and crystallises when a small quantity of water is added to the solution; it is converted into a *dinitrotetrahydronaphthol*, yellow prisms, m. p. 112—114°, when treated in aqueous solution with concentrated nitric acid. Tetrahydro-β-naphthol is intended to serve by itself or as starting material in the preparation of drugs, disinfectants, tanning materials, dyes, and explosives. H. W.

Tautomerism of Phenols. I. Quinol. WALTER FUCHS and BENNO EISNER (*Ber.*, 1919, **52**, [*B*], 2281—2286).—It is found in the case of quinol that phenols can react with sodium hydrogen sulphite in their tautomeric form as unsaturated cyclic ketones.

Reaction slowly occurs when an aqueous solution of quinol and sodium hydrogen sulphite is heated at the temperature of boiling water, whereby *sodium* cyclo*hexane*-1 : 4-*diol*-1 : 2 : 4-*trisulphonate*, colourless needles, is formed. The sulphonic character of the product follows from the failure to obtain more than traces of sulphur dioxide from it by the action of mineral acids. The constitution of the substance is deduced from its oxidation by permanganate to succinic, oxalic, and, possibly, malic acids. cyclo*Hexane*-1 : 4-*diol*-1 : 2 : 4-*trisulphonic acid* could not be isolated in the pure condition; the specimens obtained consisted of a colourless, unstable material, m. p. 172—175° (decomp.), after previous darkening. The sodium salt can be used as a photographic developer; the possibility of its presence in the ordinary quinol developer is discussed. H. W.

Primary Aromatic Alcohols. J. ALTWEGG (U.S. Pat. 1315619).—β-Phenylethyl alcohol, b. p. 89°/4 mm., is obtained in nearly theoretical yield by adding ethylene oxide (1 mol.) to an ethereal solution of magnesium phenyl bromide (1 mol.) at 0°, maintaining the temperature below 10° during the addition, then adding dry benzene, removing the ether by distillation, adding dilute sulphuric acid after cooling, and separating the phenylethyl alcohol from the benzene by decantation.

β-p-*Tolylethyl alcohol*, b. p. 98°/3 mm., is similarly obtained from magnesium *p*-tolyl bromide. β-p-*Methoxyphenylethyl alcohol*, b. p. 121°/5 mm., is prepared with the aid of toluene instead of benzene. β-3-*Methoxy*-p-*tolylethyl alcohol*, similarly prepared, is a colourless oil, b. p. 129—130°/5 mm., with a faint, aromatic odour.

CHEMICAL ABSTRACTS.

A New Sterol. TAKEO IKEGUCHI (*J. Biol. Chem.*, 1919, **40**, 175—182).—The author has previously described a sterol which he isolated from *Lycoperdon gemmatum* (A., 1915, i, 240). He has now obtained a similar product from other fungi, namely, *Armillaria edodes*, *Hydnum asparatum*, and *Collybia shiitake*. The crystalline sterols obtained from these sources melt at 159—160°, have $[\alpha]_D^{20} = -129.23°$ to $-129.55°$, and the formula $C_{30}H_{48}O_2$. They all give the same colour reactions, which differ slightly from those characteristic for cholesterol. As the author considers these crystals represent a sterol which is present in fungi generally, he proposes to call it *mycosterol*. Mycosterol inhibits the hæmolytic action of saponin, but not so powerfully as does cholesterol. It gives a crystalline compound with digitonin, $C_{85}H_{142}O_{30}$, m. p. 242° (decomp.). *Mycosterol acetate*, $C_{32}H_{50}O_3$, has m. p. 169°. Attempts to brominate failed, so that the molecule appears to be a saturated one.

It was not found possible to prepare a phenylhydrazone, so that it would appear likely that the two oxygen atoms are both present as hydroxyl groups. Only one of these is, however, acetylated by treatment with acetic anhydride, so that the other might possibly be existent as a tertiary alcohol grouping. To gain information on this point the oxidation products of the sterol were examined. On treatment with chromic acid in acetic acid solution mycosterol yielded an oxidation *product*, $C_{30}H_{48}O_3$, m. p. 188—189°. Since this substance is neutral, it is concluded that a third hydroxyl group has been formed during the oxidation, $C_{30}H_{46}(OH)_2 \longrightarrow C_{30}H_{45}(OH)_3$. Acetylation of the oxidation product confirmed this view, for a *triacetate*, $C_{36}H_{54}O_6$, needles, m. p. 201—202°, was obtained.

J. C. D.

Synthesis in the Naphthalene Nucleus. A. MADINAVEITIA and J. PUYAL (*Anal. Fis. Quim.*, 1919, **17**, 125—129).—The synthesis of 4-methoxy-α-naphthylcarbinol is described. A current of dry hydrogen chloride was passed into a mixture of α-naphthyl methyl ether and anhydrous hydrogen cyanide in ethyl ether solution in presence of powdered zinc chloride. The precipitate formed

gave the aldehyde, $OMe\cdot C_{10}H_6\cdot CHO$ (1·4), on boiling with water. This is a liquid (b. p. 210—220°/25 mm.). On treatment with aqueous potassium hydroxide a mixture of *1-methoxy-4-naphthylcarbinol* (m. p. 35°) and 1-methoxy-4-naphthoic acid (m. p. 230°) was obtained. *4-Methoxy-α-naphthyl chloromethyl ketone*, $OMe\cdot C_{10}H_6\cdot CO\cdot CH_2Cl$, is synthesised by the action of anhydrous aluminium chloride on a mixture of α-naphthyl methyl ether and chloroacetyl chloride in carbon disulphide solution; it forms needles, m. p. 70°. The corresponding *ethoxy*-derivative obtained in a similar way has m. p. 98°, and when heated with hydrochloric acid in a sealed tube at 120° yields *α-naphthyl chloromethyl ketone*, which after recrystallisation from alcohol has m. p. 130°.

W. S. M.

Preparation of Ethylidene Esters. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 313696; from *Chem. Zentr.*, 1919, *iv*, 664—665).—*Organic* vinyl esters or mixtures of vinyl esters are heated, in the presence or absence of a catalyst, with organic or inorganic acids, under conditions in which a molecule of the acid combines with a molecule of the ester and either at the ordinary or increased pressure until the action is complete. Thus, ethylidene diacetate is obtained by boiling vinyl acetate with acetic acid in the presence of a small quantity of concentrated sulphuric acid. *Vinyl benzoate*, b. p. 203°, D^{20} 1·065, and dry hydrogen chloride yield *chloroethyl benzoate*, b. p. 134°/20 mm., D^{20} 1·172. Vinyl acetate forms *ethylidene acetate benzoate*, $CH_3\cdot CH(OAc)\cdot OBz$, with benzoic acid and *chloroethyl acetate*, $OAc\cdot CHClMe$, with hydrogen chloride. The products are generally liquid, and excellent solvents for natural and artificial resins and cellulose nitrates and acetates; they may also be used in the preparation of varnishes, films, and impregnating mixtures.

H. W.

Physiological Formation of Adrenaline and Syntheses of Phenylserine. F. KNOOP (*Ber.*, 1919, **52**, [*B*], 2266—2269).—The author criticises the views which have recently been advanced by Rosenmund and Dornsaft (this vol., i, 56) on the physiological formation of adrenaline, and points out that the production of many of the intermediate substances which they postulate is not in accordance with known physiological chemical process.

[With TOTANI.]—With the object of preparing *N*-methylserine, α-chloro-β-phenyl-lactic acid was added to a solution of methylamine; contrary to expectation, the product proved to be *β-methylamino-α-hydroxy-β-phenylpropionic acid*, long prisms, decomposing completely at 272° after slowly darkening at 250°; since the original acid contains the hydroxyl group in the β-position, it follows that it must have migrated to the α-carbon atom probably owing to the intermediate formation of phenylglycidic acid. The constitution of the new acid is deduced from its oxidation by barium permanganate to *α-methylamino-α-phenylacetic acid*, pointed prisms which sublime without melting at 270°. The latter acid is also obtained by the

action of methylamine on *α-chloro-β-acetyl-β-phenyl-lactic acid*, short, coarse prisms, m. p. 131°. H. W.

Alkamine Esters of Aminotoluic Acids and Similar Compounds. E. A. WILDMAN (U.S. Pat. 1317251).—*β-Diethylaminoethyl 3-amino-p-toluate* is obtained by reducing with tin, alcohol, and hydrochloric acid at 35° the product of reaction of β-diethylaminoethyl alcohol (1 mol.) and 3-nitro-*p*-toluoyl chloride (1 mol.), removing the tin with hydrogen sulphide, and precipitating the oily ester with sodium carbonate. It forms a *hydrochloride*, colourless crystals, m. p. 157—158°. The *dimethylaminoethyl* ester (*hydrochloride*, m. p. 139—140°) and various other alkamine esters of aminotoluic acids may be prepared similarly. They act as local anæsthetics, having but slight irritating or toxic action.
CHEMICAL ABSTRACTS.

Trimorphism of *allo*Cinnamic Acids. A. W. K. DE JONG (*Vers. Akad. Wetensch. Amsterdam*, 1919, **27**, 1219—1231).—The residue obtained by evaporating a dilute solution of either of the *allo*cinnamic acids, m. p. 58° and 68°, yields the acid, m. p. 42°, at the ordinary temperature, but this acid is never obtained when concentrated solutions of the former two are used at the ordinary temperature. Aqueous solutions of the acids, m. p. 58° and 68°, yield only the acid, m. p. 58°, at −10°, but yield either of the acids at −16°. Freezing experiments, with special precautions to prevent inoculation by nuclei, were also performed, and the conclusion is drawn that the three *allo*cinnamic acids are trimorphous forms. CHEMICAL ABSTRACTS.

Anæsthetic Alkamine Esters of Alkyloxyaminobenzoic [Aminoalkyloxybenzoic] Acids. E. A. WILDMAN (U.S. Pat. 1317250).—These esters, having properties similar to those of the esters described above, are prepared in an analogous manner. *Aminoethyl m-aminoanisate* is an oil which forms a *hydrochloride*, m. p. 160°. CHEMICAL ABSTRACTS.

Salosalicylide and the Polymeric Salicylides. G. SCHROETER (*Ber.*, 1919, **52**, [*B*], 2224—2237).—The salicylides, which have hitherto been described by Anschütz, in particular that obtained by crystallisation from chloroform, show a varying molecular weight, since cryoscopic determinations in phenol or nitrobenzene indicate the formula $\left(C_6H_4<\begin{matrix}CO\\|\\O\end{matrix}\right)_4$ and ebullioscopic determinations in chloroform or nitrobenzene indicate $\left(C_6H_4<\begin{matrix}CO\\|\\O\end{matrix}\right)_2$; the author now describes the preparation of a salicylide which undoubtedly has the constitution $C_6H_4<\begin{matrix}CO\cdot O\\O\cdot CO\end{matrix}>C_6H_4$, and is therefore analogous to the dianthranilide obtained by Schroeter and Eisleb (A., 1909, i, 575). The immediate cause of publication is the recent

communication of Anschütz (this vol., i, 48) on a new disalicylide, which in many respects appears to be identical with the author's salosalicylide, although slight discrepancies are shown in the m. p. of the two substances and of their derivatives.

Salicylosalicylic acid, in spite of the presence of the free phenolic hydroxy-group, is smoothly converted by thionyl chloride into *salicylosalicylyl chloride*, $OH\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot COCl$, m. p. 99°, which is converted in the usual manner into the corresponding *anilide*, long needles, m. p. 160·5°, p-*phenetidide*, m. p. 154°, *methyl* ester, m. p. 88°, and *glycine* ester, m. p. 90—91°; the latter substance is readily hydrolysed, and, on further treatment with alkali, yields salicylic and salicyluric acid or *ethyl salicylurate*, $OH\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, needles, m. p. 88°. Salosalicylide is most conveniently prepared by boiling salicylosalicylyl chloride dissolved in benzene with diethylaniline; the dried, crystalline product has m. p. 234° when rapidly heated, but, after crystallisation from nitrobenzene, the m. p. is constant at 214—217°, whilst from benzene, a product, m. p. 204—208°, is obtained, the cause of these variations being unexplained. Cryoscopic and ebullioscopic determinations of the molecular weight in nitrobenzene and cryoscopic determinations in phenol show the substance to have the formula $C_{14}H_8O_4$.

A series of comparative experiments with salosalicylide and the so-called "chloroform–salicylide" (tetrasalicylide) is described, in all of which the latter behaves as the more stable substance. Thus, salosalicylide is converted by boiling glacial acetic acid into salicylosalicylic acid, whilst "chloroform–salicylide" remains unchanged. Similarly, the former rapidly yields methyl salicylosalicylate with methyl-alcoholic hydrogen chloride, whilst the latter is unaffected. Salicylosalicylanilide and salicylosalicyl-*p*-phenetidide are immediately obtained from salosalicylide and the requisite amine, whereas "chloroform–salicylide" can be boiled for hours with aniline without suffering alteration. Methyl alcohol containing sodium methoxide converts both salicylides into methyl salicylate. Concentrated sulphuric acid, alone and also in the presence of nitrobenzene, converts salicylosalicylic acid, salosalicylide, and "chloroform–salicylide" into salicylic acid; if the action is rapidly interrupted, it is found that the free acid is most rapidly, the "chloroform–salicylide" least rapidly, affected. Acetic anhydride and sulphuric acid convert salicylosalicylic acid into acetylsalicylosalicylic acid, the same product being mainly formed from salosalicylide; "chloroform–salicylide," however, yields *acetyltetrasalicylic acid*,

$$OAc\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

m. p. about 120°. Concentrated nitric acid converts salosalicylide into nitrosalicylic acid: under analogous conditions, chloroform–salicylide is but little affected, but nitration occurs with a mixture of nitric and sulphuric acids, *nitrosalicylide*, $\left(NO_2\cdot C_6H_3{<}\begin{matrix}CO\\O\end{matrix}\right)$ m. p. 265°, being formed. Protracted action of nitric acid on "chloroform–salicylide" in the presence of nitrobenzene leads to the formation of a *nitrotetrasalicylic acid.*

Methyl tetrasalicylate is obtained as an uncrystallisable, viscous, yellow mass by the action of salicylosalicylyl chloride on the sodium compound of methyl salicylosalicylate; the possible conversion of the ester into a tetrasalicylide has not yet been fully studied.

H. W.

Phthalic Anhydride. II. The Melting Point of Pure Phthalic Anhydride. The System: Phthalic Anhydride-Phthalic Acid. K. P. Monroe (*J. Ind. Eng. Chem.*, 1919, **11**, 1116—1119).—Pure phthalic anhydride was prepared by subliming the product obtained by the oxidation of naphthalene in a vacuum apparatus in the presence of phosphoric oxide. The melting points of the first and second sublimates agreed. Phthalic acid was estimated by a method of differential titration, in which the sample was dissolved in acetone and the solution titrated with standard normal potassium phthalate with bromophenol-blue (tetrabromophenolsulphonephthalein) as indicator. The sublimed preparations contained less than 0·1% of phthalic acid. The melting point was determined in a double-walled glass vessel immersed in a bath of sulphuric acid, and, after fusion, the temperature was gradually lowered to the point of incipient crystallisation. The equilibrium point of crystals and liquid was 130·84°. Mixtures of phthalic anhydride and acid tested in the same apparatus gave a eutectic temperature of 129·74°. By graphical interpolation, the melting point of pure phthalic acid was indicated to be 208°±2°. [See, further, *J. Soc. Chem. Ind.*, 1920, 57A.] C. A. M.

Phthalic Anhydride. III. The System: Naphthalene-Phthalic Anhydride. K. P. Monroe (*J. Ind. Eng. Chem.*, 1919, **11**, 1119—1120).—The freezing points of mixtures of pure naphthalene and phthalic anhydride were determined by the method previously described (preceding abstract), the eutectic point (26·9°) corresponding with 29·0% of phthalic anhydride. There was no evidence of the existence of solid solutions. The freezing points on the phthalic anhydride curve were calculated by means of the formula $C=(-T_0T\log_{10}x)/\Delta t$, where C is a constant, x the mol. fraction of anhydride in the mixture, T_0 the freezing point of pure phthalic anhydride, T the freezing point of the mixture, and $\Delta t=T_0-T$. The calculated values of C in this equation, based on the experimental values of T, averaged 1199. And since $L=RC/0{\cdot}4343$, where L represents the molar heat of fusion of naphthalene (4560 cal.) and R the gas constant (1·9852 cal. per degree), the molar heat of fusion of phthalic anhydride=5480 cal.

C. A. M.

Phloroacetophenone. Kiemud Behari Sen and Praphulla Chandra Ghosh (T., 1920, **117**, 61—63).

Reactivity of Diphenylketen with the Nitrile Group. Adolfo González (*Anal. Fis. Quim.*, 1919, **17**, 130—135).—Diphenylketen was mixed in sealed exhausted tubes with various

ubstances containing the group ·C:N. After remaining for wenty-four or forty-eight hours at 30° or 60°, the contents of the ubes were dissolved in aqueous ether. The ether then evaporated, and the residue dissolved in alcohol. This solution of diphenylacetic acid, formed by the action of the water on the residual diphenylketen, was titrated with barium hydroxide solution. The nitriles of acetic, benzoic, and toluic acids showed only a feeble reaction with diphenylketen in the order named. Experiments with cinnamonitrile, ethylcarbamine, dimethylcyanamide, and diethylcyanamide showed that these substances also reacted to a small extent only. With cyanogen bromide, a dense liquid was obtained, after evaporation of the excess of cyanogen bromide, which yielded a yellow polymerisation product of diphenylketen. *Hydrogen cyanide and cyanogen itself did not react with diphenylketen.* W. S. M.

Some New Bicyclic Ketones. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1919, **169**, 1168—1171).—Using the method previously described (A., 1919, i, 447) with calcium hydride, the authors have prepared the following bicyclic ketones.

4′-*Methyl*-1 : 1′-cyclo*hexylidene*-3-*methyl*cyclo*hexan*-6-*one*,

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C:C<\begin{matrix}CO\text{---}CH_2\\CH_2\cdot CHMe\end{matrix}>CH_2,$$

b. p. 185°/50 mm., D^{16} 0·9659, n_D^{16} 1·4968, gives an *oxime*, m. p. 155°, and, on reduction with hydrogen in the presence of platinum, using Vavon's method, gives p-*methyl*cyclo*hexyl*-3-*methyl*cyclo*hexan*-6-*one*, $C_7H_{13}\cdot C_7H_{11}O$, b. p. 170—175°/50 mm., D^{24} 0·947, n_D^{24} 1·4852, yielding an *oxime*, m. p. 123—124°.

2′-*Methyl*-1 : 1′-cyclo*hexylidene*-3-cyclo*hexan*-2-*one*,

$$CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2\text{---}CH_2\end{matrix}>C:C<\begin{matrix}CO\cdot CHMe\\CH_2\text{---}CH_2\end{matrix}>CH_2,$$

b. p. 175°/40 mm., D^{12} 0·9926, n_D^{12} 1·500, gives an *oxime*, b. p. 160—165°/20 mm., and a *semicarbazone*, m. p. 177—178°. On reduction by Vavon's method, it yields 2′-*methyl*-1 : 1′-cyclo*hexyl*-3-*methyl*cyclo*hexan*-2-*one*, b. p. 166—169°/35 mm., D^{12} 0·9748, n_D^{12} 1·4974, giving an *oxime* difficult to purify. Either of these ketones when reduced by sodium in absolute alcohol yields 2′-*methyl*cyclo*hexyl*-3-*methyl*cyclo*hexan*-2-*ol*, b. p. 165—168°/40 mm., D^{13} 0·973, n_D^{13} 1·5034, giving an *allophanate*, m. p. 223°.

2′ : 4′-*Dimethyl*-1 : 1′-cyclo*hexylidene*-3 : 5-*dimethyl*cyclo*hexan*-2-*one*, $CHMe<\begin{matrix}CH_2\cdot CHMe\\CH_2\text{---}CH_2\end{matrix}>C:C<\begin{matrix}CO\text{---}CHMe\\CH_2\cdot CHMe\end{matrix}>CH_2$, b. p. 184—185°/40 mm., D^{19} 0·956, n_D^{19} 1·493, gives an *oxime*, an oil, and when reduced by sodium in absolute alcohol yields 2′ : 4′-*dimethyl*-1 : 1′-cyclo*hexyl*-3 : 5-*dimethyl*cyclo*hexan*-2-*ol*, b. p. 188—191°/40 mm., D^{16} 0·945, n_D^{16} 1·496, giving an *allophanate*, m. p. 232°. W. G.

The Constitution of Dypnopinacone and its Derivatives. MAURICE DELACRE (*Ann. Chim.*, 1919, [ix], **12**, 150—178. Compare A., 1914, i, 1068; 1916, i, 679).—This paper, which should really

precede the theoretical paper previously published (compare A 1918, i, 539), deals with the inter-relationship and preparation the isomeric homodypnopinacones and homodypnopinacolins ar their transformations. It is an elaboration of work previous published (compare A., 1896, i, 591, 662). W. G.

Chlorothiolanthraquinones. K. FRIES and G. SCHÜRMAN (*Ber.*, 1919, **52**, [*B*], 2170—2181).—A continuation of previou work (A., 1912, i, 1005).

Derivatives of 2-Thiolanthraquinone [with K. ROSS].—2-Amin anthraquinone is diazotised in concentrated sulphuric acid solutio and the diazonium sulphate is converted by potassium ethyl xanthat into *ethyl 2-anthraquinonylxanthate*, yellow needles, m. p. 151° from which 2-thiolanthraquinone (Gattermann, A., 1912, i, 998) i obtained by the action of alcoholic potassium hydroxide solution *2-Chlorothiolanthraquinone*, yellow, prismatic crystals, m. p 136°, is obtained by chlorination of the corresponding thiol o disulphide in chloroform solution, and is a highly reactive sub stance; with alcoholic potassium hydroxide solution it appears t yield a solution of potassium 2-anthraquinonesulphenate, but th corresponding acid could not be isolated. When boiled with acetone it gives *2-acetonylthiolanthraquinone*,

$$C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot CH_2\cdot COMe,$$

yellow prisms, m. p. 165°, whilst with aniline in benzene or chloro form solution it forms *2-anilinothiolanthraquinone*, orange needles m. p. 171°. When a solution of the chlorothiol in chloroform i shaken with water it gives *2-anthraquinosulphenic anhydride*, small colourless crystals, m. p. 260° (decomp.), which is also produce when the chloride is boiled with alcohol.

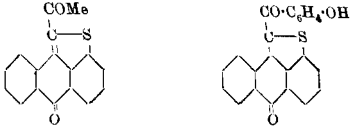
Derivatives of 1-Thiolanthraquinone.—Di-1-anthraquinonyl disul phide (compare Gattermann, *loc. cit.*) is most conveniently prepare by treatment of an alcoholic solution of 1-chloroanthraquinone with aqueous sodium disulphide, and is transformed into the correspond ing thiol by the action of dextrose and sodium hydroxide.

1-Bromothiolanthraquinone reacts readily with ammonia aniline, and dimethylaniline respectively, yielding the correspond ing *amide*, orange needles, which do not melt below 300° and ar converted by boiling acetic acid into *peri*-anthraquinone-1:9-thi azole (Gattermann, *loc. cit.*), *anilide*, shining, red needles, m. p 210°, and p-*dimethylaminophenyl* derivative, red needles, m. p 285°. With ethyl sodioacetoacetate, 1-bromothiolanthraquinone yields the *compound*,

$$C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot CH(CO_2Et)\cdot COMe,$$

yellow needles, m. p. 163°, which when boiled with mineral acid passes into the *substance* (I), yellow, prismatic crystals, m. p. 175° Similar ring formation occurs when an alkali salt of 1-thiolanthra quinone is treated with *w*-chloro-*p*-hydroxyacetophenone, the *pro*

duct (II) crystallising in golden leaflets, m. p. 258°, and yielding a red *sodium* salt. On the other hand, sodium 1-anthraquinone-



(I.) (II.)

sulphenate reacts normally with *p*- and *o*-nitrobenzyl chlorides, yielding 1-*anthraquinonyl* p-*nitrobenzyl sulphide*, orange leaflets, m. p. 243°, and 1-*anthraquinonyl* o-*nitrobenzyl sulphide*, orange needles, m. p. 251°; attempts to eliminate water from these compounds with the formation of a thiophen ring were unsuccessful. Resorcinol and 1-bromothiolanthraquinone gave 1-*anthraquinonyl* 4-*resorcyl sulphide*, orange needles, m. p. 232°.

1-Anthraquinonyl phenyl sulphide, m. p. 185°, is formed by the action of benzene on 1-chlorothiolanthraquinone in the presence of aluminium chloride, and is identical with the product obtained by Gattermann (*loc. cit.*) from *a*-nitroanthraquinone and phenyl mercaptan.

The action of ethyl sulphate on an aqueous-alcoholic solution of sodium anthraquinonesulphenate leads to the formation of 1-*anthraquinonyl ethyl sulphoxide*, yellow needles, m. p. 180° (decomp.), the constitution of which follows from its conversion by acetic and hydrobromic acids into 1-anthraquinonyl ethyl sulphide, m. p. 183° (Gattermann, *loc. cit.*); on the other hand, the free acid, when suspended in alcohol and treated with ethyl sulphate, is transformed into the corresponding ethyl ester, m. p. 149° (Fries, *loc. cit.*).

H. W.

4-Aminoanthraquinone-1-sulphenic Acid. K. FRIES and G. SCHÜRMANN (*Ber.*, 1919, **52**, [*B*], 2182—2195).—The only sulphenic acid which has hitherto been isolated in the pure condition is 1-anthraquinonesulphenic acid (Fries, A., 1912, i, 1005); in their endeavour to isolate further examples of this class of substance the authors now describe attempts to prepare the corresponding 4-hydroxy-, 4-methoxy-, and 4-amino-compounds, which, however, are not entirely successful.

4-*Bromo*-1-*hydroxyanthraquinone*, coarse, orange-yellow needles, m. p. 197°, is prepared by the action of bromine on a hot solution of 1-hydroxyanthraquinone in glacial acetic acid in the presence of sodium acetate. (It forms a red *sodium* salt, which is sparingly soluble in water.) Under similar conditions, but with double the amount of bromine, 2:4-*dibromo*-1-*hydroxyanthraquinone*, orange needles, m. p. 235°, is produced. 4:4′-Dihydroxydi-1-anthraquinonyl *disulphide*, reddish-brown, flat prisms, m. p. above 300° (compare Gattermann, A., 1912, i, 998), is conveniently prepared by the

action of an aqueous solution of sodium disulphide on 1-bromo-4-hydroxyanthraquinone dissolved in alcohol, and is reduced by dextrose to *4-hydroxy-1-thiolanthraquinone*, red needles, m. p. 194° (methyl thio-ether, shining, red leaflets, m. p. 217°, whereas Gattermann (*loc. cit.*) records 194°; *sulphoxide* of *methyl thio-ether*, orange-reddish leaflets, m. p. 226°). *Di-4-hydroxy-1-anthraquinonyl monosulphide* crystallises in red, intertwined needles, m. p. above 300°, whilst the corresponding *sulphoxide* forms slender, yellow needles, m. p. 287°. Di-4-hydroxy-1-anthraquinonyl disulphide is oxidised by hydrogen peroxide in sulphuric acid solution to *4-hydroxyanthraquinone-1-sulphonic acid*, yellowish-brown needles, m. p. 220° (the *sodium* and *ammonium* salts are sparingly soluble in cold water and crystallise in reddish-brown leaflets with metallic glance), and by nitric acid to *3-nitro-4-hydroxyanthraquinone-1-sulphonic acid*, yellow, rhombic prisms, m. p. 278°, after darkening above 255° (the *sodium*, *ammonium*, and *potassium* salts dissolve sparingly in cold water and form shining, yellow leaflets). *4-Hydroxyanthraquinone-1-sulphonyl chloride*, golden-yellow leaflets, m. p. 246°, is obtained in place of the expected chlorothiol when a suspension of the disulphide in chloroform or glacial acetic acid is treated with chlorine; the corresponding *anilide* forms shining, yellow needles, m. p. 199°.

1-*Bromo-4-methoxyanthraquinone*, pale yellow needles, m. p. 195°, is obtained by methylation of the hydroxy-compound with methyl sulphate, and is converted by sodium disulphide into di-4-methoxy-1-anthraquinonyl disulphide, yellow needles, m. p. 285° (compare Gattermann, *loc. cit.*); the latter is not attacked by bromine, and is transformed by chlorine into a sulphonic chloride, which was not further investigated; *4-methoxy-1-anthraquinonyl methyl sulphide*, orange-red needles, m. p. 187°, is prepared by reduction of the disulphide, followed by methylation of the thiol so produced.

Di-4-amino-1-anthraquinonyl disulphide, m. p. above 300° (compare Gattermann, *loc. cit.*), is conveniently prepared from 4-chloro-1-aminoanthraquinone and sodium disulphide, and is readily reduced to the corresponding thiol, which could not be isolated owing to its unusual susceptibility to oxidation. It is transformed by chlorine into *3-chloro-4-aminoanthraquinone-1-sulphonyl chloride*, orange-red needles, m. p. 230°, when rapidly heated after darkening above 200°; the corresponding *acid* forms slender, orange-yellow needles, m. p. (anhydrous) 217° (decomp.) (the *ammonium* salt forms red needles, m. p. about 304°, whilst the *anilide*, coarse, brownish-red crystals, has m. p. 210°). The sulphonic group is displaced by bromine with formation of *3-chloro-1-bromo-4-aminoanthraquinone*, m. p. 217°. 4-Amino-1-chlorothiolanthraquinone is obtained in an impure condition by the action of bromine on aminoanthraquinonyl disulphide, or, preferably, by the reduction of aminoanthraquinonesulphinic acid by hydrobromic and acetic acids; it is thus obtained as an unstable hydrobromide, orange-yellow needles, which decompose

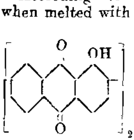
above 200°; mineral acid is removed by contact with alcohol or aqueous acetic acid, but the free amino-compound is too unstable to be isolated. The nature of the hydrobromide is established by the formation from it of the *sulphonanilide*, coarse, reddish-violet needles, m. p. 180° (decomp.), and of *4-amino-1-anthraquinonyl resorcyl sulphide*, brownish-violet leaflets, m. p. 247°. *Potassium 4-aminoanthraquinone-1-sulphenate*, dark green needles with metallic glance, is prepared from the bromothiol, but attempts to isolate the pure sulphenic acid failed; the constitution of the salt, however, is established by its conversion into *4-amino-anthraquinonyl methyl sulphoxide*, slender, red needles, m. p. 234°, which is reduced by hydrobromic and glacial acetic acids to 4-amino-anthraquinonyl methyl sulphide, m. p. 210° (compare Gattermann, *loc. cit.*), and by its oxidation to *4-aminoanthraquinonesulphinic acid*, red needles, m. p. 191° (decomp.), which forms a sparingly soluble *potassium* salt. H. W.

Certain Metallic Derivatives of Hydroxyanthraquinones. M. L. CROSSLEY (*J. Amer. Chem. Soc.*, 1919, **41**, 2081—2083).—Hydroxyanthraquinones, such as alizarin, anthrapurpurin, and flavopurpurin, form copper, cadmium, nickel, and iron salts when boiled in an organic solvent with the corresponding metallic chlorides, anhydrous sodium acetate, and nitrobenzene. *Copper, cadmium, nickel, iron, cobalt*, and *chromium* salts of alizarin have been prepared, having the general formula $C_{14}H_6O_4M$, except in the case of the cobalt salt, which has $C_{42}H_{21}O_{12}Co$.

The *copper* and *nickel* salts of anthrapurpurin and flavopurpurin were also prepared. These alizarin salts dye wool a pale shade of the colour which alizarin gives on wool previously mordanted with the corresponding metallic salt. W. G.

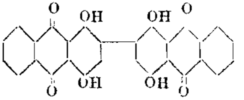
Oxidative Formation of Hydroxydianthraquinonyls from Hydroxyanthraquinones. II. Experiments with Erythro-hydroxyanthraquinone and Quinizarin. R. SCHOLL, E. SCHWINGER, and O. DISCHENDORFER (*Ber.*, 1919, **52**, [*B*], 2254—2261).—The formation of tetrahydroxydianthraquinonyl by the action of hypochlorite on an alkaline solution of alizarin (this vol., i, 64) does not appear to be an example of a general reaction. Further examples, however, are indicated in the patent literature in the cases of erythrohydroxyanthraquinone and quinizarin.

According to D.R.-P 167461, erythrohydroxyanthraquinone, when melted with potassium hydroxide, yields the hydro-compound of a substance, $C_{28}H_{14}O_6$, of unexplained constitution; this is now shown to be 1:1′-dihydroxy-2:2′-dianthraquinonyl (annexed formula), since when distilled with zinc dust in a hydrogen vacuum it gives 2:2′-dianthryl and when heated in carbon dioxide at 500° it gives *2:2′-dianthraquinonylene-1:1′-oxide*, greenish-yellow needles. The product appears to be



formed by the action of air on the aqueous solution of the melted mass, and not during the process of melting.

Quinizarin, according to D.R.-P. 146223, is converted by salts of weak acids into two compounds, $C_{28}H_{14}O_8$ and $C_{28}H_{12}O_8$, the first of which is described as giving a soluble blue sodium salt, whilst the latter yields a bluish-violet, insoluble sodium salt. It is now shown that only the acid which forms an insoluble sodium salt is a new substance, and that it has the composition $C_{28}H_{14}O_8$, whilst the other product is a mixture of this acid with quinizarin. The substance is now shown to be 1 : 4 : 1′ : 4′-*tetrahydroxy*-2 : 2′-*dianthraquinonyl* (annexed formula), since it gives 2 : 2′-dianthryl when distilled with zinc dust and a furan derivative when melted with zinc chloride.



A. G. Perkin and W. H. Perkin (T., 1888, **53**, 831) have described the isolation of three substances, $C_{28}H_{14}O_6$, $C_{28}H_{14}O_7$, and $C_{14}H_6O_4$, by the distillation of sodium anthraquinone-2-sulphonate; the first of these has been submitted to distillation with zinc dust whereby anthracene and 2 : 2′-dianthryl are obtained, but the result does not throw any definite light on the constitution of the substance. H. W.

Isomeric Carvomenthols and Scission of Inactive Carvomenthol into the Optical Antipodes. I. and II. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 82—85, 134—137).—The author prepares pure, inactive carvomenthol by reducing carvone by means of zinc dust and sodium hydroxide, transforming the dihydrocarvone thus obtained into the isomeric carvenone by heating it with dilute sulphuric acid, and reducing the carvenone by means of sodium and alcohol. From this inactive carvomenthol, the lævo-isomeride may be isolated by crystallisation of the less soluble of the two carvomenthol strychnine phthalates and conversion of this into *l*-carvomenthol hydrogen phthalate, and the latter into *l*-carvomenthol. The carvomenthol hydrogen phthalate prepared from the mother liquors of the above strychnine salt is syrupy, but, when treated with the calculated proportion of ammonia and with silver nitrate, it yields insoluble silver *d*-carvomenthol phthalate, and from this, by way of sodium *d*-carvomenthol phthalate and *d*-carvomenthol hydrogen phthalate, *d*-carvomenthol may be isolated.

l-*Carvomenthol strychnine phthalate*,

$$C_{10}H_{19}\cdot CO_2\cdot C_6H_4\cdot CO_2\cdot C_{21}H_{22}O_2N_2,$$

forms colourless needles, m. p. 155—156°, $[\alpha]_D$ −14·76° (in alcohol).

l-*Carvomenthol hydrogen phthalate*, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{10}H_{19}$, forms crystals, m. p. 125°, $[\alpha]_D$ −3·80° (in alcohol).

l-*Carvomenthol*, $C_{10}H_{19}\cdot OH$, forms an oily, limpid liquid with a faint odour of peppermint, b. p. 218° (corr.), D^{15} 0·9082, n_D^{15} 1·461, $[\alpha]_D$ −1·82°.

Silver d-*carvomenthol phthalate* is obtained as a voluminous, white precipitate, and may be purified by crystallisation from absolute alcohol or by precipitation from chloroform solution by addition of alcohol and ether.

d-*Carvomenthol hydrogen phthalate* forms slender, colourless, needles, m. p. 109°, $[\alpha]_D$ +4·62° (in alcohol).

d-*Carvomenthol* has b. p. 218° (corr.), D^{15} 0·9074, n_D^{15} 1·463, $[\alpha]_D$ +1·83°. T. H. P.

Reduction Products of Pulegone: Pulegol. I. and II. V. Paolini (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 190—192, 236—239).—Pulegol (compare Tiemann and Schmidt, A., 1897, i, 198), which previously has not been obtained free from menthol, has been prepared pure by the author.

The products formed by reducing pulegone by means of sodium and alcohol contain about 30% of a yellow resin, $C_{20}H_{34}O_2$, which appears to be identical with the bispulegone obtained by reducing pulegone with aluminium amalgam (compare Harries and Roeder, A., 1900, i, 183), and is of unknown constitution, although it is evidently a mixture of optical isomerides, possibly of ketonic (pinacone) character.

The mixture of alcoholic compounds separated from the reduction products of pulegone by distillation in a current of steam was esterified in the cold with phthalic anhydride (compare A., 1911, i, 730), the various hydrogen phthalates thus formed being separated by crystallisation and converted into the corresponding alcohols. In this way, *l*-menthol of peppermint oil, a solid *d*-menthol, and *l*-pulegol were isolated.

l-*Menthol hydrogen phthalate*, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{10}H_{19}$, forms tufts of soft, white needles, m. p. 107—108°, $[\alpha]_D$ −107·5°. The corresponding *l*-menthol is a crystalline solid, m. p. 44°, b. p. 214° (corr.), $[\alpha]_D$ −49·7°. l-*Menthol strychnine phthalate*,

$$CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{10}H_{19},C_{21}H_{22}O_2N_2,$$

forms soft, white needles, m. p. 157—158°, $[\alpha]_D$ −44·46°.

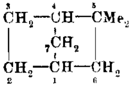
d-*Menthol strychnine hydrogen phthalate* forms crystals, m. p. 207—208°, $[\alpha]_D$ −11·7°. d-*Menthol hydrogen phthalate* forms crystals, m. p. 107—108°, $[\alpha]_D$ +18·4°. d-*Menthol*, $C_{10}H_{20}O$, is a solid and has m. p. 88—89°, b. p. 214°, and $[\alpha]_D$ +21·8°; it is a saturated componnd, and is possibly identical with the α-pulegomenthol obtained by Haller and Martine (A., 1905, i, 533) by reducing pulegone by Sabatier's method.

Pulegol hydrogen phthalate, $C_{10}H_{18}O$, crystallises in slender, white needles, m. p. 212°, $[\alpha]_D$ −86·8°. l-*Pulegol* forms slender, white needles with a faint odour of menthol, m. p. 46—47°, $[\alpha]_D$ −54·6°; it is an unsaturated compound, and readily decolorises permanganate and bromine solution, the *bromide*, $C_{10}H_{16}OBr_2$, being a dense, colourless, oily liquid. T. H. P.

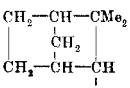
Transpositions in the Camphene Series. G. Langlois (*Ann. Chim.*, 1919, [ix], **12**, 193—264).—In the first part of the

paper, a brief résumé is given of the chemistry of camphene ai its derivatives. A closer study has been made of halogenation · this series, and the constitution of the monochloro- and monobrom derivatives of camphene has been established, and a new meth of synthesis for the introduction of carbon containing substituen into the side-chain has been found.

A general outline of the work is given, and the experiment work is to be published later. A new method of nomenclature advocated for the camphene series based on the hypothetic camphenylane (formula I) and the hypothetical radicl camphenylene (formula II) and camphenylidene (formula III



(I.)



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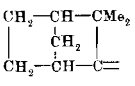


(III.)

In this system, camphene becomes camphenylidene-6-methane.

W. G.

Chemical Investigation of Various Natural Lacquer RIKO MAJIMA (*J. Tokyo Chem. Soc.*, 1919, **40**, 91—126. Compa A., 1908, i, 437; 1909, i, 402, 945; 1912, i, 883).—Chinese lacqu (*from Rhus vernicifera, Dc.*) *is essentially the* same as Japane lacquer; both contain urushiol. Yunan lacquer (from *R. succ danea*, L. fils), Formosan lacquer (from *Semecarpus vernicifera* and Ivy lacquer (from *R. toxicodendron* ?) contain *laccol*, $C_{23}H_{36}($ a homologue of urushiol. *Hydrolaccol*, $C_{17}H_{35}\cdot C_6H_3(OH)_2$ [2:; m. p. 63—64°, forms a *dimethyl ether*, m. p. 43—44°, a *mononit* derivative, m. p. 75—76°, and *dinitro*-derivative, m. p. 86—87 *Burmese lacquer contains thitsiol*, $C_{23}H_{36}O_2$. *Hydrothitsiol*,

$$C_{17}H_{35}\cdot C_6H_3(OH)_2\ [3:4],$$

m. p. 94—96°, forms a dimethyl ether, m. p. 56—57°, and mor nitro-derivative, m. p. 75—76°; the dinitro-derivative is diffic *to prepare. Hydrothitsiol is therefore very similar to isohydr* urushiol, and probably belongs to the same group. Unli urushiol and laccol, thitsiol contains a group which is hydrogenat or ozonised only with difficulty.

Siam lacquer is probably a mixture of Yunan and Burm lacquers. Korean lacquer is assumed to be identical with Japan lacquer.

CHEMICAL ABSTRACTS.

Bromination and Constitution of Caoutchouc. W. SCHMITZ (*Gummi Zeit.*, 1919, **34**, 167—169, 193—195).—Purifi rubber which has been "depolymerised" by heating with xyle under a pressure of 15 atmospheres forms an additive compour $C_{20}H_{32}Br_{10}$, when brominated in carbon tetrachloride; this produ gradually eliminates hydrogen bromide, with formation of a micı crystalline *compound*, $C_{20}H_{30}Br_8$, which is insoluble in carbon tetı

chloride and is quite distinct from the ordinary "caoutchouc tetrabromide." The decabromide is probably an open-chain compound, and it is uncertain whether the disruption of the cyclic caoutchouc molecule occurs during bromination or in the previous depolymerisation. In the bromination of solutions of ordinary rubber, the chemical process is complicated by colloidal phenomena which are absent in the case of the depolymerised hydrocarbon. [See also *J. Soc. Chem. Ind.*, 1920, 73A.] D. F. T.

Preparation of Double Compounds of Caffeine with Alkali Salts of Acetylsalicylic [*o*-Acetoxybenzoic] Acid. CHEMISCHE FABRIK J. A. WÜLFING (Brit. Pat. 136187).—*o*-Acetoxybenzoic acid (2 mols.), an alkali carbonate (1 mol.), and caffeine (1 mol.) are homogeneously mixed, and the mixture is moistened with an alcohol, ester, ketone, or chlorinated hydrocarbon of the aliphatic series to the consistency of a viscous paste, which is kneaded until a sample dissolves in water to a clear solution without the liberation of carbon dioxide. The solvent is then removed by evaporation at a low temperature, and the product, consisting of the *o*-acetoxybenzoate of caffeine and the alkali metal, is finally dried in a vacuum. G. F. M.

Syntheses in the Cinchona Series. II. Quaternary Salts. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 2090—2120).—The authors have prepared a number of quaternary salts from the different cinchona alkaloids with a view to a study of their bactericidal or, more specifically, pneumococcidal powers. The methochlorides, the benzyl chlorides, and the salts formed with the chloroacetyl derivatives of ammonia, the lower aliphatic amines, and benzylamine have been prepared. In the case of the chloroacetyl derivatives of the aromatic amines, the new series of salts with the alkaloids were only sparingly soluble in cold water, the other salts named above being, in general, fairly readily soluble. Solutions of all of the salts, aliphatic or aromatic, gave immediate precipitates with solutions of picric acid or potassium dichromate.

The quaternary salts of the alkaloids with the chloroacetyl derivatives of the aliphatic and aromatic amines were prepared by boiling equimolecular amounts of the components in dry acetone for five to seven hours. The following salts are described.

Cinchonine gives a *methochloride* decomposing at 270°, $[\alpha]_D^{22.5}$ +225·1°; a benzylochloride, m. p. 280° (decomp.), $[\alpha]_D^{22}$ +164·8°; an *iodoacetamide*, decomposing at about 190°; a *chloroacetamide*, m. p. 110—120° (decomp.), $[\alpha]_D^{25}$ +174·2°.

Cinchonidine gives a methochloride, m. p. 232—233° (decomp.), $[\alpha]_D^{22}$ −142·7°; a *chloroacetamide*, m. p. about 190°, $[\alpha]_D^{22.5}$ −112·5°.

Quinine gives a methochloride, m. p. 196—198°, $[\alpha]_D^{20}$ −211·7°; a benzylochloride, m. p. 183—188°, $[\alpha]_D^{22}$ −230·5°; an *iodoacetamide*, m. p. 175—180°, $[\alpha]_D^{23}$ −152·2°; a *chloroacetamide*, m. p. 190° (decomp.), $[\alpha]_D^{25}$ −159·6°; a *chloroacetanilide*, m. p. 224—225°

(decomp.), $[\alpha]_D^{23·5}$ $-131·5°$ (in alcohol), giving a *hydrochloride*, m.
204—206° (decomp.), and a *nitrate*, m. p. 201—203° (decomp
*quinine-*p*-chloroacetylaminophenol*,

$C_{20}H_{24}O_2N_2,CH_2Cl·CO·NH·C_6H_4·OH$,

m. p. 205° (decomp.), *quinine-*o*-chloroacetylaminobenzam*
$C_{20}H_{24}O_2N_2,CH_2Cl·CO·NH·C_6H_4·CO·NH_2$, m. p. 178—1
(decomp.), $[\alpha]_D^{25}$ $-164·4°$ (in alcohol).

Quinidine gives a *methochloride*, m. p. 250—251° (decom
$[\alpha]_D^{21}$ $+253·1°$; a *benzylochloride*, m. p. 180° (decomp.), [α
$+219·9°$; an *iodoacetamide*, m. p. 190° (decomp.), $[\alpha]_D^{22·5}$ $+166·2°$
alcohol); a *chloroacetamide*, m. p. 205° (decomp.), $[\alpha]_D^{22}$ $+207·$
an *iodoacetylcarbamide*, m. p. 170—175° (decomp.), and a *chlo*
acetylcarbamide, m. p. 176—178° (decomp.), $[\alpha]_D^{26·5}$ $+170·9°$.

Hydroquinine gives a methiodide, m. p. 233—235° (decom
$[\alpha]_D^{20·5}$ $-107·6°$ (in alcohol); a methochloride, m. p. 172—1
(decomp.), $[\alpha]_D^{21·5}$ $-162·9°$; a *benzylochloride*, m. p. 202—203
(decomp.), $[\alpha]_D^{23}$ $-196·9°$; an *iodoacetamide*, m. p. 18
$[\alpha]_D^{23·5}$ $-121·5°$ (in alcohol); a *chloroacetamide*, m. p. 1
(decomp.), $[\alpha]_D^{23}$ $-129·1°$; a *chloroacetomethylamide*,

$C_{20}H_{26}O_2N_2,CH_2Cl·CO·NHMe$,

m. p. 160°; a *chloroacetoethylamide*, m. p. 160°; a *chloroaceto*
methylamide; a *chloroacetodiethylamide*, m. p. 209—210° (decom
$[\alpha]_D^{27·5}$ $-84·8°$; a *chloroacetobenzylamide*,

$C_{20}H_{26}O_2N_2,CH_2Cl·CO·NH·CH_2Ph$,

m. p. 197—198°, $[\alpha]_D^{23}$ $-42·5°$; a *chloroacetanilide*, m. p. 2
(decomp.), $[\alpha]_D^{24}$ $-95·9°$ (in alcohol), giving a *hydrochloride* an
dinitrate; a m-*nitrochloroacetanilide*, m. p. 195—200° (decomp.)
m-*chloroacetylaminoacetanilide*, m. p. 150° (decomp.); a p-*chlo*
acetylaminoacetanilide, m. p. 205°; a p-*chloroacetylaminodimeth*
aniline, $C_{20}H_{26}O_2N_2,CH_2Cl·CO·NH·C_6H_4·NMe_2$, m. p. 2
(decomp.), $[\alpha]_D^{18·5}$ $-82·9°$ (in alcohol); a p-*chloroacetylaminodieth*
aniline, m. p. 190—195°, $[\alpha]_D^{20}$ $-80·5°$ (in alcohol); an o-*chlo*
acetylaminophenol, m. p. 185° (decomp.); a m-*chloroacetylami*
phenol, m. p. 205°, $[\alpha]_D^{21}$ $-115·7°$ (in alcohol), giving a *hyd*
chloride, m. p. 200°; *hydroquinine-*p*-chloroacetylaminophe*
hydrochloride, m. p. 196—197°; *hydroquinine-4-chloroacetylam*
catechol hydrochloride,

$C_{20}H_{26}O_2N_2,CH_2Cl·CO·NH·C_6H_3(OH)_2,HCl$,

m. p. 196—198° (decomp.); *hydroquininechloroacetyl-*o*-anisid*
m. p. 185°, $[\alpha]_D^{23}$ $-72·5°$ (in alcohol); *hydroquininechloroacety*
anisidine, m. p. 190°, $[\alpha]_D^{23}$ $-102·9°$ (in alcohol), giving a *hyd*
chloride, m. p. 170—171°; *hydroquininechloroacetyl-*p*-anisid*
m. p. 190°, $[\alpha]_D^{20}$ $-93·9°$ (in alcohol), giving a *hydrochloride*, m
180—184°; *hydroquininechloroacetyl-*o*-phenetidine*, m.
170—172°; *hydroquininechloroacetyl-*m*-phenetidine hydrochlor*
m. p. 173—174°; *hydroquininechloroacetyl-*p*-phenetidine*, m.
210°, $[\alpha]_D^{27·5}$ $-89·1°$ (in alcohol); *hydroquinine-4-chloroacetylam*
guaiacol, $C_{20}H_{26}O_2N_2,C_6H_3(OH)(OMe)·NH·CO·CH_2Cl$, m. p. 2
(decomp.); *hydroquinine-3:4-methylenedioxychloroacetanilide*,

$C_{20}H_{26}O_2N_2,CH_2O_2:C_6H_3·NH·CO·CH_2Cl$,

m. p. 185°; *hydroquinine-3:4-dimethoxychloroacetanilide*, m. p. 205—210° (decomp.); *hydroquinine-m-chloroacetylaminobenzenesulphonamide*, $C_{20}H_{26}O_2N_2,CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2\cdot NH_2$, m. p. 200—205° (decomp.).

Hydroquinidine gives an *iodoacetamide*; a *chloroacetamide*, m. p. 210° (decomp.), $[\alpha]_D^{22}$ +179·9°; *hydroquinidine-p-chloroacetylaminophenol*, m. p. 285°, giving a *hydrochloride*, m. p. 245—250° (decomp.); *hydroquinidinechloroacetyl-p-anisidine*, m. p. 260—265° (decomp.), giving a *hydrochloride*, m. p. 196—200° (decomp.).

Hydrocupreine gives a *chloroacetanilide hydrochloride*, m. p. 213—214° (decomp.), and a *chloroacetyl-p-anisidine hydrochloride*, m. p. 210° (decomp.).

Ethylhydrocupreine gives a *methochloride*, m. p. 198—199°, $[\alpha]_D^{22}$ −176·7°, and *iodoacetamide*, m. p. 185°, $[\alpha]_D^{22}$ −115·4° (in alcohol); a *chloroacetamide*, m. p. 195°, $[\alpha]_D^{22}$ −114·8°; a *p-chloroacetylaminophenol*, m. p. 178—182°, $[\alpha]_D^{22}$ −71·8° (in alcohol), giving a *hydrochloride*, m. p. 196—197°; *ethylhydrocupreinechloroacetyl-p-anisidine*, m. p. 200°, $[\alpha]_D^{25}$ −69·0° (in alcohol), giving a *hydrochloride*, m. p. 204—205° (decomp.); *ethylhydrocupreinechloroacetyl-p-phenetidine*, m. p. 210° (decomp.), $[\alpha]_D^{25.5}$ −75·25° (in alcohol), giving a *hydrochloride*, m. p. 208° (decomp.).

Most of the melting points given above are only approximate, as the substances turn to jellies long before they become fluid.

W. G.

Synthesis in the Cinchona Series. III. Azo-dyes derived from Hydrocupreine and Hydrocupreidine. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1919, **41**, 2131—2147).—Both hydrocupreine and hydrocupreidine behave in a normal manner as phenolic compounds, and yield well-defined azo-dyes with diazotised aromatic amines, and the authors assume that position 5 in the quinoline nucleus is the place of entrance of the azo-group (compare Giemsa and Halberkann, A., 1919, i, 342). In general, the benzeneazo- and tolueneazo-dyes, as well as those with *m*-substituents in the benzene ring, dye silk various shades of orange. *o*- and *p*-Alkoxy-groups deepen these colours towards the red, whilst the dyes from the naphthylamines dye silk a deep rose colour. These substances have the property of dyeing unmordanted cotton. Many of the substances described below are highly bactericidal *in vitro*. The following azo-dyes have been prepared:

Benzeneazohydrocupreine, m. p. 130°, giving a *dihydrochloride*, m. p. 181—183° (decomp.); *o-tolueneazohydrocupreine*, m. p. 110—130° (decomp.); *m-tolueneazohydrocupreine*, m. p. 125—130°, giving a *dihydrochloride*, m. p. 195° (decomp.); *p-tolueneazohydrocupreine*, m. p. 202—205°; *α-naphthaleneazohydrocupreine*, m. p. 146—149° (decomp.); *β-naphthaleneazohydrocupreine*, m. p. 240—244° (decomp.); *dibenzene-p-bisazohydrocupreine*, m. p. 204° (decomp.); *m-nitrobenzeneazohydrocupreine*, m. p. 150·5—151·5°; *p-nitrobenzeneazohydrocupreine*, m. p. 220° (decomp.); *m-acetyl-*

aminobenzeneazohydrocupreine, m. p. 155—180°; m-*carbamidobenzeneazohydrocupreine*, m. p. 165—185° (decomp.); p-*aminobenzeneazohydrocupreine*, m. p. 155—165°; p-*acetylaminobenzeneazohydrocupreine*, m. p. 158—162° (decomp.); p-*carbamidobenzeneazohydrocupreine*, decomposing at 190°; p-*hydroxybenzeneazohydrocupreine*, m. p. 150—160° (decomp.); p-*benzoyloxybenzeneazohydrocupreine dihydrochloride*, m. p. 185—195° (decomp.); 2-*methoxybenzeneazohydrocupreine*, m. p. 120°; 3-*methoxybenzeneazohydrocupreine*, m. p. 188—190°; 4-*methoxybenzeneazohydrocupreine*, m. p. 213—215° (decomp.); 2-*ethoxybenzeneazohydrocupreine*, m. p. 135—140°; 3-*ethoxybenzeneazohydrocupreine*, m. p. 90—125°; 4-*ethoxybenzeneazohydrocupreine*, m. p. 156—161°; 3 : 4-*methylenedioxybenzeneazohydrocupreine*, m. p. 177—184°; 3 : 4-*dimethoxybenzeneazohydrocupreine*, m. p. 110°; 3-*methoxy*-4-*ethoxybenzeneazohydrocupreine*, m. p. 100—135°; 4-*methoxy*-5-*ethoxybenzeneazohydrocupreine*, m. p. 75—120°; 3 : 4-*dimethoxy*-6-*carboxybenzeneazohydrocupreine*, m. p. 236° (decomp.); o-*phenylglycollic acid*-p-*azohydrocupreine*,

$$CO_2H\cdot CH_2\cdot O\cdot C_6H_4\cdot N:N\cdot C_{19}H_{23}O_2N_2,$$

m. p. 199—200° (decomp.); m-*carboxylamidobenzeneazohydrocupreine*, m. p. 195° (decomp.), gives a *dihydrochloride*; *p*-sulphobenzeneazohydrocupreine, m. p. 252° (decomp.) (compare Giemsa and Halberkann, *loc. cit.*), gives a scarlet *sodium* salt; m-*sulphonamidobenzeneazohydrocupreine*, m. p. 170—190°; p-*sulphonamidobenzeneazohydrocupreine*, m. p. 155—190°; *quinolyl*-6-*azohydrocupreine*, m. p. 232—234°; *benzeneazohydrocupreidine*, m. p. 183—185°, gives a *dihydrochloride*, m. p. 220—221° (decomp.); α-*naphthaleneazohydrocupreidine*, m. p. 132—140°; p-*nitrobenzeneazohydrocupreidine*, m. p. 135—139°; p-*sulphobenzeneazohydrocupreidine*, m. p. 247° (decomp.); benzeneazo-6-hydroxyquinoline has m. p. 160—161·5°. Most of these compounds show considerable softening or sintering and darkening previous to melting. W. G.

Final Report on the Alkaloids of Gelsemium. L. E. Sayre (*J. Amer. Pharm. Assoc.*, 1919, **8**, 708—711).—The investigation was made on about 11·5 kilos. of the drug in N° 20 powder. The following alkaloids isolated as salts were obtained: sempervirine nitrate (about 3 grams), gelsemine hydrochloride (about 8 grams) gelsemidine hydrochloride (1·75 grams), and an amorphous alkaloidal chloride, which is named gelsemoidine hydrochloride. All of these are toxic. Chemical Abstracts.

Ethylmorphine Sulphate. James Leslie Thomson (*Pharm. J.*, 1920, [iv], **50**, 7).—Ethylmorphine sulphate has m. p. 207°, and crystallises with $5H_2O$; at 15·5° it dissolves in 9·5 parts of water and in 111 parts of 90% alcohol. W. P. S.

Strychnine and Brucine. VI. R. Ciusa (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 185—187).—The action of bromine on *iso*strychnine in acetic acid solution and subsequent decomposition of the perbromide yields derivatives of the tribromo-base

$C_{21}H_{21}ON_2Br_3$, in which two bromine atoms are added at a double linking as in strychnine, while the third replaces a hydroxyl group (A., 1915, i, 893). This conclusion is confirmed by the behaviour of *iso*strychnine towards (1) alcoholic hydrogen bromide in the hot, and (2) benzoyl chloride. The first of these reactions yields a crystalline compound which appears to have the formula

$$C_{17}H_{21}NBr(CO_2Et)\colon NH,HBr,$$

and is to be considered later.

The action of benzoyl chloride on *iso*strychnine suspended in 10% potassium hydroxide solution yields only a small proportion of a compound, m. p. 174°. In pyridine solution, however, the benzoylation gives *benzoyl*iso*strychnine*, $C_{21}H_{21}O_2N_2Bz$, which crystallises in colourless needles, m. p. 174°, and has the normal molecular weight in benzene solution. The benzoylation yields also the *benzoate* of the benzoyl derivative, $C_{21}H_{21}O_2N_2Bz,BzOH,H_2O$, which forms white needles, m. p. 127°. The *hydrochloride*, $C_{21}H_{21}O_2N_2Bz,HCl$, small, colourless needles, m. p. 219°; the *aurichloride*, yellow needles, m. p. 195°; and the *dichromate*, $(C_{21}H_{21}O_2N_2Bz)_2,H_2Cr_2O_7$, slender, reddish-yellow needles, were prepared and analysed. The sulphate and nitrate crystallise well, and are slightly soluble in water. T. H. P.

Strychnine Alkaloids. XXVII. Conversion of the Methylammonium Salts from Brucine and *apo*Methylbrucine into Quinones. HERMANN LEUCHS and WALTER HINTZE (*Ber.*, 1919, **52**, [*B*], 2195—2204).—The salt of the quaternary ammonium base which is readily formed by the action of methyl sulphate on brucine shows, like the alkaloid itself, the red coloration with nitric acid, which is due to the formation of quinone; the latter, however, could not be isolated in the pure state or as a salt, and was therefore immediately reduced to the corresponding quinol, which separated from solution as a mixture of *bis*apo*methylbrucine methonitrate*, $C_{21}H_{22}O_4N_2,MeNO_3,H_2O$, colourless, shining prisms, and *acid sulphate*, $C_{21}H_{24}O_5N_2Me\cdot SO_4H$, colourless, three-sided plates, in which the additional molecule of water appears to be chemically united, since it is not evolved in a vacuum at 140°. For purification the mixture of salts was transformed by 12*N*-hydrochloric acid into *bis*apo*methylbrucine methochloride*, leaflets or prisms ($+1H_2O$), prisms ($+2H_2O$), $[\alpha]_D^{17} +6{\cdot}54°$ for the monohydrated salt in aqueous solution. Oxidation of the quinol to quinone is conveniently effected with a solution of chromic acid in hydrochloric acid, whereby the *substance*, $C_{21}H_{20}O_4N_2,MeCl,H_2CrO_4$, bright red leaflets, is obtained, which is analogous to the compound derived from bis*apo*methylbrucine itself (A., 1911, i, 746). A similar oxidation is effected by heating the quinol with a solution of hydroxylamine in hydrochloric acid, when the *monoxime* of the quinone, yellow needles, is produced; this, however, has not the simplest formula, $C_{22}H_{24}O_4N_3Cl$, but contains an additional molecule of hydrogen chloride and, according to conditions, either $4H_2O$, which may be replaced in part by hydrogen chloride, or $2H_2O$. Concentrated nitric acid converts the chloride into the *nitrate*,

$C_{22}H_{24}O_4N_3(NO_3),HNO_3,2H_2O$, yellow prisms, which is hydrolysed by water to the *substance*, $C_{22}H_{24}O_4N_3(NO_3),H_2O+H_2O$, red prisms, which is re-converted by acid into the yellow nitrate. Similarly, the dichloride of the monoxime yields a hydrate,

$$C_{22}H_{24}O_4N_3Cl,H_2O,$$

slender, red needles, when the excess of hydrochloric acid is removed preferably by addition of alkali hydroxide (1 mol.). By the aid of a second molecule of alkali hydroxide, the residual chlorine atom can be removed as hydrogen chloride, and a betaine-like *compound*, $C_{22}H_{25}O_5N_3$, orange-red prisms, is produced.

The yellow nitrate of the oxime is only formed with gently warmed nitric acid. At a higher temperature a more complex action occurs in which nitration is accompanied by oxidation of the quinone-oxime or nitrosophenol group to the nitrophenol group and a molecule of water is added; the nitrate, $C_{22}H_{25}O_{11}N_5$, which is thus produced, is identical with the product of the oxidation of the oxime of methylcacotheline (following abstract), from which it is more readily produced.

In a similar manner, bis*apo*methylbrucine methochloride is converted through the quinone by $5N$-nitric acid at 50—60° into methylcacotheline methonitrate. On the other hand, only quinone formation, unaccompanied by nitration, is observed with concentrated nitric acid at 0°, so that in this instance, in contrast to that of bis*apo*methylbrucine itself (A., 1911, i, 746), it was not possible to obtain a nitrated but not hydrated quinone. H. W.

Strychnine Alkaloids. XXVIII. Transformations and the Violet Colour Reaction of Methylcacotheline. HERMANN LEUCHS and WALTER HINTZE (*Ber.*, 1919, **52**, [*B*], 2204—2224. Compare A., 1919, i, 35).—Previous investigation of the methonitrate of the cacotheline bases (now termed methylcacotheline) had established the probability that it, in accordance with its mode of formation from brucine dimethosulphate, is a nitrated and hydrated quinone, but the function of the added water was left unexplained. Further evidence of its quinonoid nature is now adduced by the isolation of a *semicarbazone* as nitrate, $C_{23}H_{27}O_7N_6\cdot NO_3,3H_2O$, the *semicarbazone* of the methochloride, slender, pale yellow needles, and the *monophenylhydrazone* as nitrate, $C_{28}H_{30}O_6N_5\cdot NO_3,3H_2O$, brownish-red, oblique prisms. To determine whether water has been added in such a manner that the acid amide group $\cdot CO-N\!\!\lt$ of brucine has been converted into $-CO_2H \mid H-N\lt$, attempts have been made to identify the presence of the carboxyl group in two ways. On the one hand, hydrogen chloride has been removed from the semicarbazone hydrochloride by the agency of silver oxide (or, in general, a molecule of acid from the salts by a molecule of alkali), whereby a crystalline betaine, $C_{23}H_{26}O_7N_6$, has been produced which readily re-forms the original salts with acids. On the other hand, the presence of the carboxyl group is shown by the conversion of the semicarbazone nitrate into its *methyl* ester, $C_{24}H_{29}O_7N_6Cl$. The phenylhydrazone only yielded an amorphous betaine, but methylcacotheline itself gave a crystalline *betaine*, $C_{22}H_{23}O_7N_3$, and, as no

other acidic group can be present, may thus be regarded as containing the carboxyl group. The chloride of the monoxime described previously (*loc. cit.*) also yielded a crystalline *betaine*,

$$C_{22}H_{24}O_7N_4,4H_2O;$$

possibly, in this instance, the oxime or the tautomeric nitrosophenol group could take part in the dehydration, but this view is rendered improbable by the isolation of a crystalline *monomethyl* and *monoethyl* ester.

The *nitrate* of the monoxime can only be obtained from the chloride by the use of metallic nitrates, since the oxime is oxidised when warmed with even *N*-nitric acid, the quinoneoxime or nitrosophenol group being converted into the nitrophenol group, a second nitro-group being thus introduced into the molecule; this '*dinitrophenol*' also yields a crystalline *betaine*, $C_{22}H_{24}O_8N_4$, whilst its salts can be reduced to a '*diaminophenol*,' $C_{22}H_{29}O_4N_4Cl,2HCl$ or 1HCl, which can be obtained less smoothly from the nitroquinonemonoxime. According to these reactions, the formula of methylcacotheline may be resolved thus: $C_{18}H_{17}\{-CO-CO-; \vdots C\cdot NO_2; NMeNO_3; \equiv NH; \cdot CO_2H; \equiv CH(OH)\}$.

The violet coloration caused by the action of stannous chloride or sulphur dioxide on methylcacotheline has been previously investigated and attributed to the conversion of the quinone into the corresponding quinol, the necessary hydrogen being regarded as obtained by the conversion of the secondary alcoholic group of the brucine molecule into the keto-group. Further examination has now been made on the action of methylcacotheline and similar salts towards sulphur dioxide in the presence of mineral acids; methylcacotheline itself yields a crystalline, dark violet *nitrate*, which, however, contains two hydrogen atoms more than the original salt into which it is re-converted by nitric acid,

$$C_{22}H_{24}O_{10}N_4 \underset{HNO_3}{\overset{SO_2}{\rightleftarrows}} C_{22}H_{26}O_{10}N_4;$$

the corresponding chloride, $C_{22}H_{24}O_7N_3Cl$, similarly yields a violet *quinol*, $C_{22}H_{26}O_7N_3Cl$, from which it is re-formed by ferric chloride. The behaviour of the acid sulphate is precisely similar, the quinol sulphate re-forming the original material on treatment with ferric sulphate. The sulphite thus occupies a peculiar position in that reduction in this case only is caused by hydrogen derived from within the molecule. The presence of acid radicles which are not ionised is not essential to the production of the violet colour, since they can be removed by warming with one (or two) molecules of alkali, whereby deep violet *betaines* are obtained:

$$C_{22}H_{26}O_7N_3\cdot NO_3 \longrightarrow C_{22}H_{25}O_7N_3.$$

With the object of demonstrating the presence of the phenol group in the violet quinols, the violet chloride was boiled with acetic anhydride and sodium acetate; the *product*, however, did not contain the acetyl group, but was formed by loss of a molecule of hydrogen chloride and of water from the original substance. It appears to have a betaine structure, since it readily yields additive products with acids, and probably is a phenol betaine.

Reduction of the betaine anhydride, $C_{22}H_{23}O_6N_5$, with tin and hydrochloric acid yields the aminoquinol, $C_{22}H_{26}O_4N_3Cl,HCl,2H_2O$, previously obtained from methylcacotheline and formulated with $1H_2O$. A molecule of water appears to be eliminated during the reduction of methylcacotheline in a manner similar to that observed during the action of acetic anhydride on the violet quinol. The composition of the amine hydrochloride varies considerably, and the following forms have been prepared and analysed:

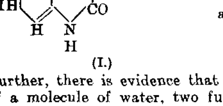
$$C_{22}H_{28}O_5N_3Cl,HCl,$$

needles; $C_{22}H_{28}O_5N_3Cl,2H_2O$, trapezoidal tables;

$$C_{22}H_{28}O_5N_3Cl,HCl,$$

rectangular or quadratic tables; from the first of these, hydrogen chloride is eliminated at 100°, whilst the third is stable at this temperature. H. W.

The Chemical Identification of Thyroxin. II. E. C. KENDALL and A. E. OSTERBERG (*J. Biol. Chem.*, 1919, **40**, 265—334).—Thyroxin, the physiologically active constituent of the thyroid gland (A., 1919, i, 497), can exist in two tautomeric forms. The *keto*-form (I), which is by far the more stable, crystallises in long needles, m. p. 250°; the enol form (II) crystallises in rosettes of needles, m. p. 204°. From a consideration of the chemical behaviour of the substance, so far as it is yet known, the authors suggest the formulæ



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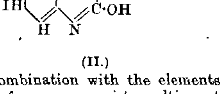
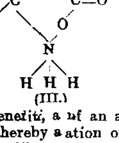
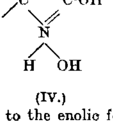


(I.) (II.)

Further, there is evidence that by combination with the elements of a molecule of water, two further forms may exist, melting at 225° (III) and 216° (IV) respectively, the suggested nature of which is indicated by the partial formulæ



(III.)



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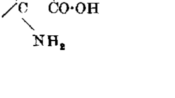


(V.)

geneiti, a nf an acid to the enolic form leads to fission of the ring whereby a ation of an amino-acid (V), of which III is an internal readily for the evidence on which the authors base these formulæ, he original must be consulted.

The *acetyl* derivative crystallises in short, curved needles, m. p. 228—235° (decomp.). The *sulphate* has the formula

$$C_{22}H_{22}O_{10}N_2I_6S.$$

The hydrochloride crystallises in star-shaped plates. When treated with cyanic acid, thyroxin yields a *carbamyl* derivative,

$$C_6H_4I_3<\begin{matrix}C(C_2H_4\cdot CO_2H)\\ N(CO\cdot NH_2)\text{—}\end{matrix}>CO.$$

Many mono- and di-basic metallic salts of thyroxin have been prepared, but although they are beautifully crystalline, they have not been obtained in a pure condition. A *dimethyl* ester has been prepared, and is hydrolysed to a *monomethyl* ester by alkali hydroxides.

Thyroxin is not easily oxidised or reduced. When exposed to sunlight in weak alkaline solution, it is very unstable. Within twenty-four hours, the solution turns pink or yellow, deepening to a brown, and an aromatic odour is produced. The development of the pink colour is accompanied by the splitting off of iodine in the form of hypoiodous acid. J. C. D.

Constitution of Arylanthranils, Lactimides, and Lactimones. GUSTAV HELLER and HILDE LAUTH (*Ber.*, 1919, **52**, [*B*], 2295—2303).—In a previous communication (Heller, A., 1915, i, 844) it has been shown that acylanthranils react with hydrazine hydrate in alcoholic solution to yield 3-hydrazino-3-aryl-3:4-dihydrobenzoxazones, and the reaction is interpreted as in favour of the formula $\begin{matrix}CO\text{—}\\ C_6H_4\end{matrix}>N\cdot COR$ for the acylanthranils, the behaviour being difficult to reconcile with the alternative formula $C_6H_4<\begin{matrix}CO\cdot O\\ N{=}CR\end{matrix}$. A number of somewhat similarly constituted compounds have now been examined.

Anthranoylanthranilic anhydride and acetylanthranoylanthranilic anhydride (Schroeter, A., 1917, i, 529, 620) are converted by hydrazine hydrate in warm alcoholic solution into 3-*hydrazino-3-o-aminophenyl-3:4-dihydrobenzoxazone*, pale yellow needles, m. p. 200° (decomp.), and 3-*hydrazino-3-o-acetylaminophenyl-3:4-dihydrobenzoxazone*, colourless, thread-like crystals, m. p. 216° (decomp.); these substances are decomposed by alkali, and, on acidification with acetic acid, the lactone is re-formed in a somewhat impure condition. It appears, therefore, that complex acylanthranyls contain the same ring as is present in the simpler substances.

Benzoylaminocinnamic lactimide and acetylaminocinnamic lactimide react similarly with hydrazine hydrate, yielding, respectively, 5-*keto-2-hydrazino-2-phenyl-4-benzylidenetetrahydro-oxazole*,

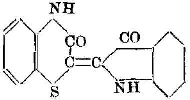
$$\begin{matrix}CO\text{————}O\\ C(:CHPh)\cdot NH\end{matrix}>CPh\cdot NH\cdot NH_2,$$

colourless needles, m. p. 153—154° (*benzylidenehydrazino*-derivative, colourless needles, m. p. about 220° after darkening from 145°), and 5-*keto-2-hydrazino-2-methyl-4-benzylidenetetrahydro-oxazole*, coarse crystals and clusters of needles, m. p. about 180°

(decomp.) after darkening from 160°. For reasons similar to those advanced in the case of the acylanthranils, the original substances must have the constitution $CHPh:C<\begin{matrix}CO\\ |\\ N\cdot CO\cdot R\end{matrix}$.

a-Benzoylaminoisobutyric anhydride (Mohr and Geis, A., 1908, i, 339; 1910, i, 117) is transformed by hydrazine hydrate into *5-keto-2-hydrazino-2-phenyl-4:4-dimethyltetrahydro-oxazole*, slender needles, m. p. 134°, and must therefore have the lactam formula. The isomeric *a-benzoylaminoisobutyric hydrazide*, obtained by the action of hydrazine hydrate on the acid chloride, has m. p. 248° (decomp.). H. W.

Dyes Derived from Ketodihydro-1 : 4-benzisothiazine. W. Herzog (*Ber.*, 1919, **52**, [*B*], 2270—2274).—Ketodihydrobenzothiazine reacts with a-isatinanilide in a solvent of high boiling point, such as ethyl benzoate, to yield *2(2'-indoxyl)-3-ketodihydro-1 : 4-benzisothiazine* (annexed formula), dull, brownish-violet needles with metallic glance, m. p. above 300°, which dyes cotton bluish-violet and wool reddish-violet. *2(2'-Thionaphthen)-3-ketodihydro-1:4-benzisothiazine*, yellow, silky needles, m. p. above 300°, prepared similarly from thionaphthenquinoneanilide, has little affinity for the textile fibres. β-Isatinanilide yields *2(3'-indoxyl)-3-ketodihydro-1 : 4-benzisothiazine*, orange-red, silky needles, m. p. about 270°, which has very little affinity for the textile fibres.



The inferiority of the substances as dyes in comparison with indigo-blue and thioindigo-red is readily interpreted according to the Clauss hypothesis, since they contain only one quinonoid indogen, whilst the latter dyes contain two such groups. H. W.

Certain Arylamino-derivatives of 4(5)-Methyl-5(4)-aminomethylglyoxaline and the Syntheses of 4(5)-(β-p-Hydroxyphenylethyl-β-aminoethyl)glyoxaline. Otto Gerngross (*Ber.*, 1919, **52**, [*B*], 2304—2318).—The anil of 4(5)-methylglyoxaline-5(4)-aldehyde (Gerngross, A., 1912, i, 314) is reduced by sodium in boiling isoamyl-alcoholic solution in an atmosphere of hydrogen to *4(5)-methyl-5(4)-anilinomethylglyoxaline*, $CH\begin{matrix}\lessdot NH\cdot CMe\\ \lessdot N—C\cdot CH_2\cdot NHPh\end{matrix}$, slender needles from water, m. p. 183° (corr.) [*hydrochloride*, four-sided leaflets, m. p. 201° (corr.) after becoming discoloured at 175° and softening at 195°]; the corresponding *benzoyl* derivative crystallises in shining, four-sided plates, m. p. 206° (corr.), yields a *hydrochloride*, m. p. 235° (corr.), and does not couple with diazobenzenesulphonic acid in alkaline solution. The preparation of the aniline derivative is only conveniently effected in this manner when very small quantities of material are required; for larger

amounts, it is more conveniently produced by the action of aniline (2 mols.) on a solution of methylchloromethylglyoxaline hydrochloride (1 mol.) in methyl alcohol (compare Ewins, T., 1911, **99**, 2054); under these conditions, its formation is accompanied to a greater or less extent by that of N-*phenyliminobis*-4 : 5-*dimethylglyoxaline*, $NPh\left(CH_2\cdot C{\lessgtr}{\begin{array}{l}CMe\cdot NH\\N{=\!=}CH\end{array}}\right)_2$, small needles, m. p. 199—200° (corr.), from which it can be readily separated by taking advantage of the very sparing solubility of the latter in boiling acetone.

[With Hans Nast.]—The synthesis of 4(5)-(β-p-*hydroxyphenylethyl*-β-*aminoethyl*)*glyoxaline*,

$$CH{\lessgtr}{\begin{array}{l}NH\cdot CH\\N{-\!-}C\cdot C_2H_4\cdot NH\cdot C_2H_4\cdot C_6H_4\cdot OH\end{array}},$$

is described, which is of pharmacological interest, since it contains the active principles of *Secale cornutum* and tyramine united to one another. 5(4)-β-*Phenylethylaminomethyl*-4(5)-*methylglyoxaline* is obtained by slowly adding a solution of the hydrochloride of 4(5)-methyl-5(4)-chloromethylglyoxaline in methyl alcohol to β-phenylethylamine dissolved in slightly methyl-alcoholic water; the crude product is converted successively into the *dipicrate*, prisms, m. p. 211° (corr.) after softening at 204°, and the *dihydrochloride*, shining, hygroscopic, crystalline leaflets, m. p. 254° (corr.; decomp.) [*aurichloride*, yellow crystals, m. p. 215° (corr.)]. Small quantities of β-*phenylethyliminobis*-4 : 5-*dimethylglyoxaline*,

$$(C_3H_2N_2Me\cdot CH_2)_2N\cdot C_2H_4\cdot Ph,$$

are produced during this reaction, and this substance becomes the main product when care is not taken to maintain a constant excess of the amine; the *tripicrate*, shining, yellow crystals, m. p. 176° (corr.) after softening at 160°, the hygroscopic *hydrochloride*, and the *platinichloride*, which darkens above 200°, but does not melt below 270°, are described. Similarly, the hydrochloride of methylimidazolylmethyl chloride and *p*-phenylenediamine yield 5(4)-p-*aminoanilinomethyl*-4(5)-*methylglyoxaline*,

$$C_3H_2N_2Me\cdot CH_2\cdot NH\cdot C_6H_4\cdot NH_2,$$

the *trihydrochloride*, four-sided, rhombic plates, m. p. 257° (decomp.), and *dipicrate*, large, yellow crystals, m. p. 219—220° (decomp.), of which are described.

β-Aminoethylglyoxaline condenses with *p*-hydroxyphenylethyl chloride in methyl-alcoholic solution at 100° to yield 4(5)-(β-p-*hydroxyphenylethyl*-β-*aminoethyl*)*glyoxaline*; the crude product is treated with hydrochloric acid to remove the excess of the histamine base, and is purified by successive conversion into the *dipicrate*, m. p. 203·5° (corr.; decomp.), the *dihydrochloride*, colourless rods, m. p. 202—203° (corr.), and the free base, microscopic, four-sided prisms, m. p. 157° (corr.); the *monohydrochloride* forms four-sided platelets, m. p. 195° (corr.). H. W.

Quinazolines. XXXIV. The Synthesis of certain Nitro- and Amino-benzoyleneureas [Diketotetrahydroquinazolines] and some Compounds Related Thereto. MARSTON TAYLOR BOGERT and GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1919, **41**, 2052—2068).—A supplement to, and an elaboration of, work previously published (compare A., 1916, i, 672), certain new compounds being described. Methyl anthranilate, when condensed with potassium *iso*cyanate in acetic acid solution, yielded *methyl* o-*carbamidobenzoate*, m. p. 177—177·5° (corr.). 6-Nitro-2:4-diketo-1:2:3:4-tetrahydroquinazoline, m. p. 330—331° (corr.), gives a *sodium* salt, which is colourless at limit 7 on the Sörensen scale, but at 7·5 and on to 11 very slowly develops a greenish-yellow colour. The development of colour is, however, too slow for the salt to be of any use as an indicator. 6:8-Dinitrodiketotetrahydroquinazoline (*loc. cit.*) gives *potassium* and *ammonium* salts which resemble the sodium salt in general behaviour, except that the ammonium salt decomposes without explosion. The authors find higher m. p.'s for certain quinazoline derivatives than did Abt (compare A., 1889, 609). Thus 2:4-dichloroquinazoline has m. p. 119·5° (corr.); 2:4-dimethoxyquinazoline has m. p. 74°; 2:4-diketo-1:3-dimethyltetrahydroquinazoline has m. p. 167—168° (corr.).

o-Carbamidobenzoic acid when nitrated with nitric acid (D 1·5) at −5° to −10° yielded 5-*nitro*-2-*nitrocarbamidobenzoic acid*,

$$NO_2\cdot NH\cdot CO\cdot NH\cdot C_6H_3(NO_2)\cdot CO_2H,$$

which it was very difficult to purify. Its *methyl* ester, decomposing at 184—185° (corr.), was obtained by nitration of methyl *o*-carbamidobenzoate. In an endeavour to clear up the chemistry of 5-nitro-2-acetylaminobenzoic acid, the authors have prepared a specimen, m. p. 218° (corr.), and its *barium, calcium, ferric, copper, lead*, and *silver* salts. Similarly, they prepared 5-nitro-2-aminobenzoic acid, m. p. 278° (corr.; decomp.), and its *sodium, potassium*, and *ammonium* salts. It gives a *methyl* ester, m. p. 168° (corr.).

The proof that the compound obtained by Bogert and Geiger (compare A., 1912, i, 395, 510) by the nitration of 4-quinazolone is 6-nitro-4-quinazolone is supplied by the preparation of the same compound by fusing together 5-nitroanthranilic acid and formamide. W. G.

New Type of Substances Derived from Diazonium Compounds and Alkali Cyanides. GUSTAV HELLER and MARIE MEYER (*Ber.*, 1919, **52**, [*B*], 2287—2294).—When an aqueous solution of a benzenediazonium salt is added to a solution of potassium cyanide in the presence of an excess of potassium hydroxide, a yellow oil is formed, which immediately yields a colourless solution, from which an unstable, sparingly soluble, red salt gradually separates; this slowly decomposes, even in the cold liquid, with evolution of nitrogen and development of the odour of *iso*cyanide. The corresponding free compound, however, is more stable and has the formula $C_{13}H_{11}ON_5$. The colour of the substance, its failure to yield hydroxylamine when treated with acids, and its reduction by

hydrogen to a colourless derivative lead the authors to consider it to be *benzenediazoxydiazobenzenecarbimide*,

$PhN_2 \cdot C(:NH) \cdot O \cdot N_2Ph$;

confirmatory evidence is deduced from the fact that it is only formed from *syn*-benzenediazonium hydrate and salt of hydrocyanic acid, and not from the *anti*-diazotate and substances which contain the cyano-group united to carbon or nitrogen.

The *potassium* salt of benzenediazoxydiazobenzenecarbimide forms dark red leaflets, m. p. 239° (decomp.), whilst the *sodium* salt consists of bronze-like leaflets, m. p. 209° (decomp.). The *lead, mercurous, manganese, silver, copper, cobalt, bismuth, stannous, cadmium, zinc*, and *mercuric* salts are described. The corresponding free substance crystallises in red needles, m. p. 92°, with violent evolution of gas. Attempts to obtain a benzoyl or methyl derivative were unsuccessful. p-*Toluenediazoxydiazo*-p-*toluenecarbimide*, m. p. 111° (decomp.), is converted by phenylcarbimide into p-*toluenediazoxydiazo*-p-*toluenecarbimidophenylcarbamide*, $C_6H_4Me \cdot N_2 \cdot C(:N \cdot CO \cdot NHPh) \cdot O \cdot N_2 \cdot C_6H_4Me$, orange-yellow crystals, m. p. 148° (decomp.). o-*Toluenediazoxydiazo*-o-*toluenecarbimide* forms bluish-red rods, m. p. 100° (decomp.).

The sodium salt of benzenediazoxydiazobenzenecarbimide slowly decomposes in aqueous solution, yielding nitrogen, aniline, benzonitrile, ammonia, and nitrite, but not phenol. The free substance is decomposed by hot water, yielding smeary products, from which traces of phenol and benzonitrile could be isolated by distillation with steam.

The sodium salt of benzenediazoxydiazobenzenecarbimide is reduced by sodium hyposulphite in alkaline solution, by alkaline stannous chloride, by zinc dust, and acetic or hydrochloric acid in alcoholic solution, or by phenylhydrazine in alcoholic solution to *benzenediazoxyphenylhydrazinocarbimide*,

$PhNH \cdot NH \cdot C(:NH) \cdot O \cdot N_2Ph$,

colourless needles or crystalline aggregates, m. p. about 154° (decomp.), which is converted by methyl sulphate into the corresponding *methyl* derivative, m. p. 137—138° (decomp.). Protracted reduction of benzenediazoxydiazobenzenecarbimide by zinc and acid leads to the formation of aniline, whilst, in a similar manner, phenylhydrazine is formed when stannous chloride and hydrochloric acid act on a solution of the substance in glacial acetic acid. Benzenediazoxyphenylhydrazinocarbimide yields practically the same products as does the unreduced compound when it decomposes in cold alkaline solution; in acid solution, it is gradually decomposed, with the formation of phenol. o-*Toluenediazoxy*-o-*tolylhydrazinocarbimide* forms colourless crystals, m. p. 150° (decomp.). H. W.

The Special Reactions in the Transformation of the Azides of Carboxylic Acids. I.—VI. THEODOR CURTIUS (*J. pr. Chem.*, 1916, [ii], **94**, 273—382).—The "normal" reaction of the acid azides, and their formation, are summarised as follows: $\mathbf{R \cdot CO_2Et \longrightarrow R \cdot CO \cdot NH \cdot NH_2 \longrightarrow R \cdot CO \cdot N_3 \longrightarrow R \cdot NH \cdot CO_2Et}$ or

R·NH·CO·NH·R ⟶ R·NH_2, numerous examples of which have already been given in the case of mono-, di-, and even tri-carboxylic acids (most recent notices: A., 1914, i, 873; 1915, i, 124, 169, 787, 872). "Special" reactions are given by (1) the azides of acids having two –CO·N_3 groups attached to the same carbon atom, (2) by hydroxy-acids and their ethers, and (3) by α-amino- and α-acylamino-acids. In the first case, the ultimate products are generally the aldehydes or ketones produced by the hydrolysis of the methylenediamines, $CHR(NH_2)_2$ or $CRR'(NH_2)_2$. Examples are now given. The second section is dealt with in Parts VII. to XIII. of this series (A., 1917, i, 635—639), and the third section in Parts XIV. to XVII. (A., 1918, i, 44).

I. [With Wilhelm Cäsar.]—*Hydrazide and Azide of Methyl- and* iso*Amyl-malonic Acids.*—Methylmalonodihydrazide,

$$CHMe(CO{\cdot}N_2H_3)_2,$$

crystallises in silky needles, m. p. 172—173° (compare Bülow and Weidlich, A., 1906, i, 981), forms a *dihydrochloride*, m. p. 168°, a dibenzylidene compound, m. p. 251° (*ibid.*), a *disalicylidene* compound, glistening leaflets, m. p. 216—217°, a *di*iso*propylidene* compound, by boiling with acetone, minute needles, m. p. 158—159°, and a very explosive, yellow *diazide*, $CHMe(CO{\cdot}N_3)_2$. This reacts with aniline to form methylmalondianilide, m. p. 182° (Meyer and Bock, A., 1906, i, 726), and with *p*-toluidine to give the di-*p*-toluidide (Commanducci and Lobello, A., 1905, i, 271). It reacts with alcohol to form an oily urethane, which yields carbon dioxide and acetaldehyde on boiling with dilute sulphuric acid. iso*Amylmalonodihydrazide* forms silky crystals, m. p. 140° (decomp.), and gives a *dihydrochloride*, silky leaflets, a *dibenzylidene* compound, microscopic leaflets, m. p. 240°, and a *disalicylidene* compound, white tablets, m. p. 186—187°. The *diazide* is a pungent-smelling oil which reacts with aniline to give iso*amylmalondianilide*, silky needles, m. p. 185°, and with alcohol to form a urethane, this being hydrolysed by dilute sulphuric acid to *iso*hexaldehyde, C_5H_{11}·CHO. The aqueous distillate of the aldehyde reacts with benzhydrazide to give the *benzhydrazone*, C_5H_{11}·CH:N·NHBz, silky needles, m. p. 215°. *Dimethylmalonodihydrazide* crystallises in prisms, m. p. 208°, but gives poor results in the subsequent reactions, acetone being recognised, however, as the ultimate product. *Benzylmethylmalonodihydrazide* forms silky leaflets, m. p. 260°.

II. [With Heinrich Rechnitz.]—*Transformation of Ethylmalondiazide into Propaldehyde, and Transformation of Propaldazine into 4-Methyl-5-ethylpyrazoline.*—Ethylmalonodihydrazide forms slender needles, m. p. 168° (compare Bülow and Bozen-[illegible]dt, A., 1910, i, 233), and gives a *dihydrochloride*, m. p. [illegible]—181°, a *dipicrate*, yellow needles, m. p. 187° (decomp.), a [illegible]*zylidene* compound, m. p. 241—242° (decomp.), and a *disali*[illegible]*e* compound, m. p. 201°. The *diazide* is very explosive, but [illegible] converted into the dianilide and *di*-p-*toluidide*, m. p. 288°, [illegible]e diurethane, $CHEt(NH{\cdot}CO_2Et)_2$, which is hydrolysed by [illegible]huric acid to propaldehyde. The final yield is very poor,

however, as the yield of azide is only 35—40% to begin with. Propaldazine, $N_2(:CHEt)_2$, is a colourless oil with fishy odour, b. p. 143—145°, D^{19} 0·844, n_D^{18} 1·379, and it reacts with maleic acid in absolute alcohol to form *hydrazine maleate*, $N_2H_4,C_4H_4O_4$, very slender needles, m. p. 144° (decomp.), and *4-methyl-5-ethylpyrazoline*, $NH<\begin{matrix}N{=\!=}CH\\ CHEt\cdot CHMe\end{matrix}$. This is a colourless liquid with the odour of peppermint, b. p. 105—107°/18 mm., and is very stable in solution in dilute sulphuric acid. It gives blue and white precipitates with Fehling's solution and mercuric chloride respectively, but does not reduce these agents. With *p*-toluenediazonium sulphate it gives a brick-red compound, which dissolves in concentrated hydrochloric acid with deep bluish-violet colour, the solution becoming pale red on dilution. The yield of the pyrazoline is improved if the alcoholic mixture of propaldazine and maleic acid is heated, or if hydrazine maleate is mixed with propaldehyde, but the chief product in any case is a *compound*, probably of the formula $C_6H_{11}N_2\cdot CEt<\begin{matrix}CH\cdot C_6H_{11}N_2\\ CMe\cdot C_6H_{11}N_2\end{matrix}$ (4-methyl-5-ethylpyrazoline = $C_6H_{12}N_2$). This is a yellowish-red, viscous oil, b. p. 245—250°/18 mm., which turns red litmus blue, but only forms oily salts. It has the reactions of the simple 4-methyl-5-ethylpyrazoline and is apparently formed by the elimination of two molecules of ammonia from four of the pyrazoline. The alkaline liquid left after the extraction of the two bases contains an amount of ammonia which agrees with this view, and fumaric acid is also present.

III. [With OWEN E. MOTT, repeated and in part amended by WILHELM SIEBER.]—*Hydrazide and Azide of Benzylmalonic Acid.*—*Benzylmalonodihydrazide*, $CH_2Ph\cdot CH(CO\cdot N_2H_3)_2$, crystallises in slender, glistening needles, m. p. 164°, forms a *dihydrochloride*, m. p. 135°, and a *dibenzylidene* compound, small needles, m. p. 220°, and changes into *secondary benzylmalonohydrazide*, $CH_2Ph\cdot CH<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}$, glistening leaflets, m. p. 241°, when (*a*) its hydrochloride is kept in the moist condition or heated for some hours at 100°, (*b*) it is treated with alcoholic iodine, or (*c*) it is treated with sodium nitrite in the presence of a slight excess of hydrochloric acid. In the last reaction *benzylmalonyldiazide*, an explosive, yellow oil, is the chief product, and the by-product can be suppressed if an excess of acid is used. The diazide may be converted into the *dianilide*, $CH_2Ph\cdot CH(CO\cdot NHPh)_2$, m. p. 217°, and *diurethane*, $CH_2Ph\cdot CH(NH\cdot CO_2Et)_2$, a mass of very slender needles, m. p. 166°, the latter being hydrolysed by 2% sulphuric acid to phenylacetaldehyde, b. p. 81—82°/12 mm., which forms a *benzhydrazone*, $CH_2Ph\cdot CH:N\cdot NHBz$, needles, m. p. 148—149°, and a *m-nitrobenzhydrazone*, m. p. 152°.

IV. [With CARLO MARANGOLO.]—*Hydrazide and Azide of* m-*Xylylmalonic Acid* (m-*Methylbenzylmalonic Acid*).—m-*Xylylmalonodihydrazide* [m-*methylbenzylmalonodihydrazide*],

$$C_6H_4Me\cdot CH_2\cdot CH(CO\cdot N_2H_3)_2,$$

crystallises in silky needles, forms a hygroscopic *dihydrochloride*, m. p. 135—136° (decomp.), a *dibenzylidene* compound, small, glistening needles, m. p. 219°, a *disalicylidene* compound, m. p. 185—186°, a *diisopropylidene* compound, m. p. 182° (from acetone), and a *bisdiphenylmethylene* compound,

$$C_6H_4Me\cdot CH_2\cdot CH(CO\cdot NH\cdot N{:}CPh_2)_2,$$

m. p. 164° (from benzophenone). The dihydrazide changes into the *secondary* m-*methylbenzylmalonohydrazide*,

$$C_6H_4Me\cdot CH_2\cdot CH{<}\begin{matrix}CO\cdot NH\\ |\\ CO\cdot NH\end{matrix},$$

m. p. 236—237°, when treated with alcoholic iodine. The unstable *diazide* may be converted into the dianilide, m. p. 193°, *di*-p-*toluidide*, $C_6H_4Me\cdot CH_2\cdot CH(CO\cdot NH\cdot C_6H_4Me)_2$, slender needles, m. p. 190°, and crude *diurethane*, $C_6H_4Me\cdot CH_2\cdot CH(NH\cdot CO_2Et)_2$, which is hydrolysed by dilute sulphuric acid to m-*tolylacetaldehyde*, $C_6H_4Me\cdot CH_2\cdot CHO$. This is a pleasant-smelling, pale yellow, refractive oil, b. p. 99—100°/18 mm., which forms an oily *phenylhydrazone*, a *benzhydrazone*, $C_6H_4Me\cdot CH_2\cdot CH{:}N\cdot NHBz$, long needles, m. p. 129—130°, and a m-*nitrobenzhydrazone*, very pale yellow, prismatic needles, m. p. 115—116°.

V. [With GOTTFRIED GRANDEL.]—*Hydrazide and Azide of Pentane-ααεε-tetracarboxylic Acid and of* cyclo*Butane*-1 : 1-*dicarboxylic Acid.*—The ethyl esters of these acids are obtained by adding a mixture of trimethylene bromide and ethyl malonate to a mass of sodium ethoxide in alcohol. If the mixture is added rapidly and the temperature is only controlled sufficiently to prevent undue violence, the yield of the pentane derivative rises to about 12%, but if the addition and cooling are carefully controlled, the yield of cyclic compound is improved. The latter is slightly volatile in steam, and may be slowly removed in this way from the non-volatile pentane compound. In any case, the yields are poor, and the reaction cannot be fully explained. Ethyl pentane-ααεε-tetracarboxylate is a pleasant-smelling, viscous, colourless oil, b. p. 210—215°/12 mm., and ethyl *cyclo*butane-1 : 1-dicarboxylate is a limpid, highly refractive oil with the odour of camphor, b. p. 220—228° (compare Perkin, T., 1883—1891). The esters are converted into the amides and hydrazides by the action of ammonia or hydrazine in the usual way. *Pentane-ααεε-tetracarboxylamide* forms soft prisms, m. p. 280°, and the *tetrahydrazide*,

$$(N_2H_3\cdot CO)_2CH\cdot C_3H_6\cdot CH(CO\cdot N_2H_3)_2,$$

is a snowy powder, m. p. 200° (decomp.), which yields a *tetrahydrochloride*, m. p. 200°, a *platinochloride*, $C_9H_{20}O_4N_8,2H_2PtCl_4$, and a *tetrabenzylidene* compound, m. p. 248°. The *tetra-azide* is an odourless, white powder, which melts under benzene at 50—55°, is comparatively stable when dry, but explodes on rubbing. The *tetra-anilide* is obtained from the azide as a white powder, m. p. 285°. The azide also changes into an impure carbamide derivative when boiled with water, and into an oily urethane on boiling with alcohol, the latter giving a distillate containing glutardialdehyde, $C_3H_6(CHO)_2$, when boiled with dilute sulphuric acid. cyclo*Butane*-

1:1-*dicarboxylamide* crystallises in long, rectangular prisms, m. p. 268°, and the *dihydrazide*, $CH_2<\genfrac{}{}{0pt}{}{CH_2}{CH_2}>C(CO\cdot N_2H_3)_2$, forms stout tablets or short needles, m. p. 109—110°, and yields a *dihydrochloride*, m. p. 175—176° (decomp.), a *platinochloride*, B,H_2PtCl_4, a *dipicrate*, yellow needles, m. p. 185°, a *dibenzylidene* compound, m. p. 212—213°, a *disalicylidene* compound, m. p. 215°, and a *diisopropylidene* compound, m. p. 176—177°. For the conversion of the dihydrazide into the diazide, the temperature of the mixture must be kept well below $-5°$, otherwise evolution of carbon dioxide and nitrogen takes place and a deep red solution is obtained. The *diazide*, $CH_2<\genfrac{}{}{0pt}{}{CH_2}{CH_2}>C(CO\cdot N_3)_2$, is a colourless, lachrymatory oil, which can only be kept when moist for a short time as it is decomposed by water. cyclo*Butane*-1:1-*dicarboxylanilide*, m. p. 214—215°, and the *di*-p-*toluidide*, m. p. 247°, are obtained from the azide. The azide is hydrolysed to a considerable extent with the production of free hydrazoic acid when warmed with water or alcohol, but it also loses carbon dioxide and nitrogen, and when the product is acidified and distilled, *cyclo*butanone is found in the distillate. From the solution, cyclo*butanonephenylhydrazone*, a pure white, light mass of felted needles, or long needles from benzene, m. p. 95—96°, which can only be kept a few hours, and the stable semicarbazone, m. p. 211—212° (decomp.) (compare Demjanov and Dojarenko, A., 1908, i, 156), may be precipitated by adding the appropriate agents.

VI. [With HERMANN THIEMANN.]—*Hydrazide and Azide of* s.-*Ethanetetracarboxylic Acid.*—*Ethanetetracarboxytetrahydrazide*, $C_2H_2(CO\cdot N_2H_3)_4$, crystallises in slender needles, m. p. 205° (decomp.), and forms a *tetrahydrochloride*, m. p. 145—148° (decomp.), a *tetrabenzylidene* compound, m. p. 242°, a *tetrasalicylidene* compound, m. p. 213—214°, and a *tetraisopropylidene* compound, $C_{18}H_{30}O_4N_8,4H_2O$, m. p. 255°, which evolves dimethylketazine, $CMe_2{:}N\cdot N{:}CMe_2$, when heated at 110°. The conversion of the hydrazide into the *tetra-azide* (radiate groups of white crystals) only proceeds in the presence of an excess of hydrochloric acid which entails considerable loss of hydrazoic acid. The azide may be converted into the *tetra-anilide*, m. p. 240—242°, *tetra*-p-*toluidide*, m. p. 236—237°, and *tetraurethane*, $C_2H_2(NH\cdot CO_2Et)_4$, white needles, m. p. 268°, the mother liquor from the latter preparation containing glyoxal. When the tetrahydrazide is warmed with water it changes into the yellow *hydrazine* salt of *ethanetetracarboxytrihydrazide*, $NH_2\cdot N<\genfrac{}{}{0pt}{}{CO\text{———}CH\cdot CO\cdot N_2H_3}{C(O\cdot N_2H_5){:}C\cdot CO\cdot N_2H_3}$, m. p. 142°, which reacts with acetone to form the *triisopropylidene* compound, $CMe_2{:}N\cdot N<\genfrac{}{}{0pt}{}{CO\cdot CH\cdot CO\cdot NH\cdot N{:}CMe_2}{CO\cdot CH\cdot CO\cdot NH\cdot N{:}CMe_2}$ m. p. 138—140° (with $3H_2O$, m. p. 90—92°). This is converted into the *tribenzylidene* compound, m. p. 193—194°, by means of benzaldehyde, and then into the *trihydrochloride*, m. p. 182—183° (decomp.), by rubbing with

concentrated hydrochloric acid. The corresponding *triazide* is a very explosive, viscous oil, which may be converted into *ethanetricarboxytrianilide*, $NHPh\cdot CO\cdot CH_2\cdot CH(CO\cdot NHPh)_2$, m. p. 223—224°, and *tri*-p-*toluidide*, m. p. 230°. The tetrahydrazide loses still more hydrazine residues when ground with bromine water or warmed with alcoholic iodine, the product being *ethanetetracarboxydihydrazide*, $NH_2\cdot N{<}\begin{matrix}CO\cdot CH\cdot CO\\ CO\cdot CH\cdot CO\end{matrix}{>}N\cdot NH_2$, which crystallises in highly refractive, glistening scales, m. p. 254—255°. This has both acidic and basic properties, forming a *dipotassium* salt,

$$NH_2\cdot N{<}\begin{matrix}C(OK){:}C\text{——}CO\\ CO\text{——}C{:}C(OK)\end{matrix}{>}N\cdot NH_2,2H_2O,$$

pale yellow leaflets, m. p. 158°, a *dihydrazine* salt, m. p. 208°, a *diammonium* salt, m. p. 98°, which loses ammonia when kept, and a *hydrochloride*, m. p. 185—186° (decomp.). It also yields a *dibenzylidene* compound, m. p. 240—241°, a *disalicylidene* compound, m. p. 231—232°, a *diisopropylidene* compound, m. p. 261°, and a *tetraacetyl* derivative, m. p. 202—203°. When treated with sodium nitrite and hydrochloric acid, the dihydrazide changes into *ethanetetracarboxydi-imide*, $NH{<}\begin{matrix}CO\cdot CH\cdot CO\\ CO\cdot CH\cdot CO\end{matrix}{>}NH$, which crystallises in colourless leaflets, blackens at 265—270°, and forms a stable *disilver* salt, $2H_2O$. When boiled with water for a few hours, the tetra- or tri-hydrazides lose carbon dioxide as well as hydrazine and give succinodihydrazide, thus,

$$C_2H_2(CO\cdot N_2H_3)_4 + 2H_2O = C_2H_4(CO\cdot N_2H_3)_2 + 2N_2H_4 + 2CO_2.$$

J. C. W.

The Evolution of Proteins. E. L. KENNAWAY (*Chem. News*, 1920, **120**, 13—16).—After discussing the amino-acids which have been established as occurring commonly in proteins, the author draws attention to their very limited number, but great diversity, as regards structure. He then goes on to consider whether the simplest plants, for example, bacteria, yeasts, contain all these amino-acids present in the higher plants, and, taking the information available, shows that, with the exception of hydroxyproline, the presence or absence of which is not established, all the seventeen amino-acids considered are present in one or other of the five bacteria, yeast and mould, which have been examined. The two doubtful occurrences are serine and cystine. The author then discusses the bearing of these results on evolution, particularly on that of the higher animals, which are dependent on plant life for some of their essential amino-acids. W. G.

The Hydrolysis of Proteins in the Presence of Extraneous Materials and on the Origin and Nature of the "Humin" of a Protein Hydrosolate. R. A. GORTNER (*Science*, 1918, **48**, 122—124; from *Physiol. Abstr.*, 1920, **4**, 466).—A strong criticism of McHargue's statements regarding protein hydrolysis (compare A., 1918, ii, 280). W. G.

Action of Furfuraldehyde and Dextrose on Amino-acids and Protein Hydrolysates. C. T. Dowell and Paul Menaul (*J. Biol. Chem.*, 1919, **40**, 131—136).—It was observed that when whole plants, including the seed, are hydrolysed, a large amount of furfuraldehyde is given off, and that an unusually high percentage of humin nitrogen is obtained. No evidence of a reaction between glycine and furfuraldehyde was obtained, but there was an indication that reaction occurred with tyrosine and cystine. Only a slight amount of the humin nitrogen is due to adsorption. There is reaction between the hydrolysates of proteins and furfuraldehyde, which is particularly marked when the reaction takes place in neutral or acid solution. The greatest loss of amino-nitrogen occurs, however, when dextrose is present during hydrolysis, and it is therefore concluded that dextrose reacts directly with the amino-acids, and not through the intermediate formation of furfuraldehyde. Complete hydrolysis of proteins may be effected by heating in 10% hydrochloric acid for three hours at 20 lb. pressure. J. C. D.

Hydrolysis of Stizolobin, the Globulin of the Chinese Velvet Bean, Stizolobium niveum. D. Breese Jones and Carl O. Johns (*J. Biol. Chem.*, 1919, **40**, 435—448).—The globulin of the Chinese velvet bean has been hydrolysed and the percentages of the constituent amino-acids determined: 77·21% of the total protein was isolated as amino-acids and ammonia. Aspartic acid was determined both by the usual ester method and by Dakin's recently published process (Dakin, A., 1919, i, 150). The former method yielded 5·7% and the new process 9·23%. 2·81% of the recently discovered hydroxyglutamic acid was also obtained.
J. C. D.

Solubility of Casein in Dilute Solutions of Sodium Chloride and its Dependence on the Hydrogen Ion Concentration. Sigfrid Ryd (*Arkiv. Kem. Min. Geol.* 1917, **7**, No. 1, 1—15).—The solubility of casein in dilute solutions of sodium chloride has been determined for thirty-two concentrations at 18—20°. The casein in weighed quantity was placed in a cylindrical vessel fitted with stirrer, thermometer, and two burettes. A quantity of a standard solution of sodium hydroxide, sufficient to dissolve the casein, but not an excess, was added, and the mixture stirred until solution had occurred. Then from one of the burettes standard hydrochloric acid was added until an opalescence was produced. The amount of sodium hydroxide taken in the first place was so chosen that the hydrochloric acid necessary to produce opalescence was slightly more than equivalent to the sodium hydroxide, the excess of acid was neutralised, and the casein redissolved by the addition of sodium hydroxide from the other burette. This process was continued until the acid and alkali, when exactly equivalent, just produced an opalescence. Hence the concentration of the solution on casein and sodium chloride was known. The solubility of casein in sodium chloride solution rises with increase in

the concentration of the sodium chloride to a maximum, which is reached with 0·1150*N*-sodium chloride. The following are the extreme values: 0·0365*N*-NaCl dissolves 0·64 mg. per c.c., 0·1150*N*-NaCl dissolves 3·46 mg. per c.c., and 0·2725*N*-NaCl dissolves 1·32 mg. per c.c. The hydrogen-ion concentration of each saturated solution was determined at 21°, and it is found that this quantity is practically constant at $5{\cdot}13 \times 10^{-6}N$, from which it follows that opalescence in solutions of casein occurs when the hydrogen-ion concentration has the above value and this lies very near the iso-electric point, which has a value $1{\cdot}1 \times 10^{-4}$—$7{\cdot}9 \times 10^{-6}$.

J. F. S.

Hæmocyanin. I. Recrystallisation of Oxyhæmocyanin. AUREL D. CRAIFALEANU (*Boll. Soc. Nat. Napoli.*, 1918, **31**, 88—99).—The author describes the crystallisation of hæmocyanins from the blood of *Octopus vulgaris*, *O. macropus*, and *Eledone moschata*, following the methods described by Hofmeister and by Hopkins and Pinkus for the crystallisation of egg-albumin.

The hæmocyanin derived from the blood of *O. vulgaris* may crystallise in three different forms: short needles, rosettes of needles, and relatively large crystals, which, from their appearance under the microscope, the author terms "projectile" crystals. These forms vary with the conditions of crystallisation. The hæmocyanin from *O. macropus* was obtained in long, needle-shaped crystals. On allowing the glass containing the crystals and mother liquor to remain for some time, the crystals become insoluble, and this modification is termed *parahaemocyanin*. The pigment from the blood of *E. moschata* crystallises in needles. The so-called "projectile" crystals are characteristic of the hæmocyanin from *O. vulgaris*.

J. C. D.

Crystalline Salts of Uridinephosphoric Acid. P. A. LEVENE (*J. Biol. Chem.*, 1919, **40**, 395—398. Compare A., 1918, i, 130).—The normal *ammonium* salt is readily prepared from the brucine salt, and crystallises in heavy, elongated prisms, decomp. 185° (uncorr.). In aqueous solution it has $[\alpha]_D^{20}$ +21·0°, and crystallises with $1H_2O$. The *ammonium hydrogen* salt crystallises in long, prismatic needles, $[\alpha]_D^{20}$ +13·0°, contracts at 210° (corr.), decomp. at 242° (corr.). Normal *lead* salt, long needles. Brucine salt, $C_9H_{13}O_9N_2P(C_{23}H_{26}O_4N_2)_2,7H_2O$, $[\alpha]_D^{20}$ −20·0° (in very dilute solution). Air-dried substance effervesced at 185° (corr.), and contracted and melted without further decomposition at 195° (corr.).

J. C. D.

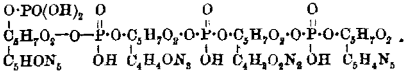
Crystalline Guanylic Acid. P. A. LEVENE (*J. Biol. Chem.*, 1919, **40**, 171—174).—The crude brucine salt of guanylic acid was converted into the ammonium salt and precipitated from aqueous solution with neutral lead acetate. The solution obtained after removal of lead from the precipitate yielded, on concentration under diminished pressure, a crystalline substance. Analysis corresponded

with the formula $C_{10}H_{14}O_8N_5,\frac{1}{2}H_2O$, $[\alpha]_D^{20}$ in aqueous solution $-7·5°$. In 5% aqueous ammonia, $[\alpha]_D^{20}$ $-43·5°$. In 10% hydrochloric acid it was optically inactive. The substance had all the properties of guanylic acid. It gelatinised in the presence of mineral impurities and turned brown at 208°. The brucine salt, $C_{56}H_{64}O_{16}N_9,7H_2O$, contracted at 217°, melted at 233°, and effervesced at 240°; $[\alpha]_D^{20}$ $-26·0°$ in 35% alcohol. J. C. D.

The Structure of Yeast-Nucleic Acid. IV. Ammonia Hydrolysis. P. A. LEVENE (*J. Biol. Chem.*, 1919, **40**, 415—424). —The original graphic representation of the entire molecule of yeast-nucleic acid had only an arbitrary schematic sense (compare Levene and Jacobs, A., 1909, i, 620, 686; 1911, i, 96, 510). The views as to structural formulæ advanced by Jones (A., 1917, 232, 233, 596, 597) and by Thannhauser (A., 1914, i, 1015; Thannhauser and Dorfmüller, A., 1918, i, 47) and the evidence adduced in their support are considered.

Nucleic acid was hydrolysed in a 2·5% aqueous ammonia solution for one hour at 100°, a milder treatment than that employed by either Jones or Thannhauser. It is proved that the adenine–uridine dinucleotide is a mixture of two mononucleotides. The fraction originally regarded by Jones as a guanine–cytosine dinucleotide was found to consist principally of guanosinephosphoric acid, together with a small proportion of uridinephosphoric acid. The present findings nullify the experimental evidence in support of the theories of Jones and Thannhauser. From the theoretical point of view, the theory of Thannhauser is weak because it assumes a carbon to carbon linking, which is a very strong type of union, whereas the polynucleotide is readily dismembered into mononucleotides. The ether linking accepted by Jones is also a very firm union.

On the basis of considerations such as these the linking of the nucleotides could be expressed most simply in the following way:



For the present this formula expresses the facts known about the structure of yeast-nucleic acid. Whether it will require alteration or not, it is certain that the polynucleotide structure of yeast-nucleic acid is definitely established. J. C. D.

The Combination of Enzyme and Substrate. I. Estimation of Pepsin. II. The Effect of the Hydrogen Ion Concentration. JOHN H. NORTHROP (*J. Gen. Physiol.*, 1919, **2**, 113—122).—The change in the conductivity during the digestion of egg-albumin by pepsin affords a convenient and accurate method for the estimation of pepsin. The changes in conductivity do not follow the actual rate of digestion, but the percentage change in conductivity is constant for a given quantity of pepsin, irrespective of the absolute value of the original conductivity. It was found

that the maximum change occurred in strong solutions of egg albumin titrated to p_H 2·6 with hydrochloric acid. By this process it is possible to determine quantitatively the amount of pepsin removed from solution by various substances.

A series of experiments with substances such as starch, calcium sulphate, agar, kaolin, blood-charcoal, caseinogen, and egg-albumin gave results which indicate that the removal of pepsin from solution is not purely a matter of surface, but that it is dependent in some way on the substance itself. That is, the equilibrium reached is *independent of the size of the particles, and therefore of their surface.* This would indicate that the process is either one of solution, in which case the law of partition-coefficients should be found to hold, or of chemical combination, in which case the law of mass action should apply.

Preliminary experiments indicate that the process follows the law of partition-coefficients.

There is a decided optimum hydrogen-ion concentration for the combination of pepsin with its substrate corresponding with the optimum reaction for digestion. It is suggested that the combination of pepsin with its substrate, and hence the rate of digestion, is governed by the quantity of ionised protein present. J. C. D.

The Different Actions of Pepsin and Chymosin on Acid Solutions of Syntonin. OLOF HAMMARSTEN (*Medd. K. Vetenskaps-akad. Nobel-Inst.*, 1919, **5**, No. 7, 1—13).—In previous papers (compare A., 1918, i, 459, 510) the author has put forward evidence in support of assigning separate identities to chymosin and pepsin. Further support to his views is given by the experiments detailed in the present paper, syntonin obtained from fish or horseflesh being used in place of acid and alkali legumin (A., 1918, i, 510). The method of experiment was similar to that previously detailed, and all the results indicate that chymosin acts on syntonin, forming albumoses, at an acid concentration at which pepsin is inactive.

T. S. P.

Catalase. EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, **40**, 514—522).—The author has previously deduced an equation (*ibid.*, **35** and **36**) by which it is possible to describe the course of the reaction between catalase and hydrogen peroxide at any temperature and any initial concentrations by using the temperature-coefficient and the value of k at 18°. He now finds that, contrary to Evans's statement (A., 1907, i, 456), even with a range of concentration from 1 to 80, k/E_0 is constant provided the hydrogen-ion concentration is kept constant. Blood catalase, prepared by the method of Senter (A., 1903, ii, 661), is diluted to less than 1%, 20 c.c. of 0·02N-sodium hydrogen carbonate are added to each solution of the enzyme, the volume is made up to 130 c.c. at 25°, and 20 c.c. of 0·028N-hydrogen peroxide are added. The estimations are made in a current of carbon dioxide.

The author discusses the kinetics of catalase action, and is of opinion that the action is purely chemical.

CHEMICAL ABSTRACTS.

Urease and the Radiation Theory of Enzyme Action. IV. H. P. Barendrecht (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 126—138. Compare A., 1919, i, 604; this vol., i, 102).—A continuation and completion of previous work. The accelerating action observed with urease and attributed by previous experimenters to carbon dioxide is shown to be non-existent. Ammonium carbonate and carbon dioxide form a powerful buffer mixture which can maintain a constant P_H value, the essential condition for constant enzyme activity in a urea solution during hydrolysis by urease. The estimation of initial velocities of hydrolysis, equal concentrations of urease being allowed to act on different concentrations of urea at constant P_H and T values, produces results which appear inexplicable without the radiation theory. The lower the value of P_H the more the initial velocities increase with increase in the urea concentration. With high P_H values there is first an increase and then a decrease on raising the urea concentration. These facts are strictly in accordance with the radiation hypothesis. The urease radiation, weakened by spreading or in any other way, may effect synthesis. This is indicated by the fact that at high P_H values, where the urease is shown to be decaying, reversion of an hydrolysis has been observed. From the last fact it is deduced that outside the sphere of hydrolytic action around a urease molecule there must be a region of radiation, weakened by spreading, and therefore of synthesis. This is confirmed by the fact that on diluting the urease concentration beyond a certain value, its specific activity is decreased. From this it is evident that the synthetic action of urease, which is not decaying, can only come into play when the spheres of hydrolytic action do not intersect one another. It is shown experimentally that in any urease solution in which the enzyme is decaying through the combined action of alkalinity, temperature, and time, a synthesis of urea from ammonium carbonate, proportional to the urease concentration, is observed. A description of an apparatus for determining the concentration of hydrogen and hydroxyl ions is included in the paper. J. F. S.

Cyanodiphenylarsine. Giuseppe Sturniolo and Giacomo Bellinzoni (*Boll. Chim. Farm.*, 1919, **58**, 409—410 *).—*Cyanodiphenylarsine*, $AsPh_2{\cdot}CN$, crystallises in almost colourless, apparently monoclinic plates, m. p. 35°, having the odour of both garlic and bitter almonds, hydrogen cyanide being liberated readily by the action of moist air; its odour irritates the nasal mucus, provoking sneezing. By treatment with aqueous or alcoholic alkali hydroxide, or by heating with water, or by distillation either in a current of steam or under reduced pressure (100 mm.), it is converted into diphenylarsine oxide, $(AsPh_2)_2O$. When treated either with concentrated nitric acid on the water-bath or with 2% hydrogen peroxide, or with bromine water in the cold, it yields diphenylarsinic acid. Both cyanodiphenylarsine and diphenylarsine oxide, containing tervalent arsenic, are transformed into diphenylarsinic acid, in

* and *Gazzetta*, 1919, **49**, ii, 326—327.

which the arsenic is quinquevalent, by the traces of hydrogen peroxide sometimes occurring as impurities in ether and in light petroleum. The alkali salts of diphenylarsinic acid are soluble, whereas the iron salt forms a very fine, white, insoluble powder and decomposes when heated. T. H. P.

Tetraphenyldiarsine. C. W. PORTER and PARRY BORGSTROM (*J. Amer. Chem. Soc.*, 1919, **41**, 2048—2051).—The authors have prepared tetraphenyldiarsine in a pure state from the oxide by the method of Michaelis and Schulte (compare A., 1883, 187), and distributed it into sealed glass tubes without allowing it to come into contact with air. So prepared, when exposed to air it oxidises to diphenylarsinic acid and tetraphenyldiarsine oxide, but is not spontaneously inflammable, as reported by Michaelis (compare A., 1902, i, 515). In benzene solution it gradually absorbs oxygen. In similar solution it rapidly absorbs iodine, giving a crystalline *iodo-compound*, m. p. 30°, which is probably diphenyliodoarsine. Its vapour pressure at 200° is about 1 mm., and at 300° in a vacuum it decomposes, giving arsenic and triphenylarsine, and consequently its molecular weight in the state of vapour cannot be determined. Molecular weight determinations by the cryoscopic method in naphthalene indicate that tetraphenyldiarsine is associated at the freezing point of naphthalene. W. G.

The Constitution of Arseno-metallic Compounds. P. KARRER (*Ber.*, 1919, **52**, [*B*], 2319—2324).—In reply to Kolle (*Deut. med. Woch.*, 1918, 1177) and Binz, Bauer and Hallstein (*Arbb. aus Inst. exp. Therapie Georg Speyer Haus*, 1919, **25**, 45), the author maintains the correctness of the views advanced by Ehrlich and Karrer (A., 1916, i, 95), that the metal in complex salts, such as copper- and silver-salvarsan, is directly united to the arsenic atom, thus, $\begin{bmatrix} R\cdot As \;.\;.\;.\;.\; Me \\ \Vert \\ R\cdot As \;.\;.\;.\;.\; Me \end{bmatrix}\begin{matrix} X \\ X \end{matrix}$. H. W.

Chemotherapeutic Studies on Organic Compounds containing Mercury and Arsenic. GEORGE W. RAIZISS, JOHN A. KOLMER, and JOSEPH L. GAVRON (*J. Biol. Chem.*, 1919, **40**, 533—552).—The following are described: 3-*Nitroarsanilic acid mercuriacetate*, $OAc\cdot Hg\cdot C_6H_2(NO_2)(NH_2)\cdot AsO(OH)_2$, bright yellow powder soluble in dilute sodium hydroxide on warming. 3-*Nitro*-4-*hydroxyphenylarsinic acid mercuriacetate*, $C_8H_8O_8NAsHg$, yellow powder soluble in dilute sodium hydroxide. 3:5-*Dinitro*-4-*hydroxyphenylarsinic acid mercuriacetate*, $C_8H_7O_{10}N_2AsHg$, bright yellow powder partly soluble in dilute sodium hydroxide. 3-*Amino*-4-*hydroxyphenylarsinic acid mercuriacetate*, $C_8H_{10}O_6NAsHg$, brown powder soluble in dilute sodium hydroxide; the solution decomposes on keeping, with deposition of metallic mercury. 3:5-*Diamino*-4-*hydroxyphenylarsinic acid mercuriacetate*, $C_8H_{11}O_6N_2AsHg$, dark brown powder soluble in very dilute sodium hydroxide; the solution

decomposes, with formation of metallic mercury. *4-Carboxyphenylarsinic acid mercuriacetate*, $C_9H_9O_7AsHg$, cream-coloured powder insoluble in dilute sodium hydroxide, soluble in dilute hydrochloric acid, concentrated sodium chloride solution, and in glacial acetic acid on warming. *Diacetyl-3:5-diamino-4-hydroxyphenylarsinic acid mercuriacetate*, $C_{12}H_{15}O_8N_2AsHg$, grey powder soluble in dilute sodium hydroxide to form a brown solution, from which mercury is deposited. *3-Bromoarsanilic acid mercuriacetate*,

$C_8H_9O_5NBrAsHg$,

white powder soluble in dilute sodium hydroxide, warm glacial acetic acid, and 10% hydrochloric acid. *3-Bromo-oxalylarsanilic acid mercuriacetate*, $C_{10}H_9O_8NBrAsHg$, white powder soluble in dilute sodium hydroxide; the solution deposits metallic mercury on keeping.

All the above compounds are insoluble in the usual organic solvents. The presence of the arsinic acid group in the molecule of organic compounds apparently does not interfere with the entrance of the mercury group. As a class, this type of compound is comparatively stable in alkaline solution, the splitting off of mercury occurring only in compounds containing an amino-group. The toxic effect on the animal body appears to be caused mainly by the mercury group. These new compounds were not found to be superior to the ordinary organic mercury compounds as regards curative influence in experimental trypanosomiasis and germicidal effect in vitro. J. C. D.

Lead Triaryl, a Parallel to Triphenylmethyl. ERICH KRAUSE and MARIA SCHMITZ (*Ber.*, 1919, **52**, [*B*], 2165—2170).—Indications of the formation of unsaturated organo-derivatives of lead, in which the metal is attached to carbon atoms by fewer than four valencies, have been previously observed, but the isolation of such substances has hitherto been impossible. The authors have succeeded in preparing lead tri-*p*-2-xylyl in the crystalline condition, and have shown that unsaturated derivatives are also formed to a greater or less extent by the action of magnesium phenyl or *p*-tolyl bromide on lead dichloride.

Lead tri-p-2-*xylyl*, $Pb(C_6H_3Me_2)_3$, is prepared by the addition of finely powdered lead dichloride to an ethereal solution of the calculated quantity of magnesium *p*-2-xylyl bromide; the bulk of the dichloride dissolves to a brownish-yellow or chestnut-brown solution of the diaryl compound, which gradually at the ordinary temperature, but more rapidly when heated, deposits lead and yields the lead triaryl. The substance forms a pale yellowish-green, heavy, crystalline powder which, under the microscope, appears to be formed of colourless, well-developed rhombs. Determinations of the molecular weight by the cryoscopic method in benzene solution indicate the formula $[(C_8H_9)_3Pb]_2$, so that the compound may possibly be regarded as hexa-*p*-2-xylyl diplumban,

$(C_8H_9)_3Pb\cdot Pb(C_8H_9)_3$.

The colour of the substance, however, points to a feeble union of

the lead atoms and to the possibility of dissociation under the influence of light. Probably the lead atoms are united in much the same manner as the methane carbon atoms of the triarylmethyls. As is to be expected, the substance is readily attacked by chemical reagents; thus, when treated with bromine in pyridine solution at $-40°$, it gives *lead tri*-p-2-*xylyl bromide*, four-sided leaflets, m. p. 177°, whilst in chloroform solution at $-10°$ it yields *lead di*-p-2-*xylyl dibromide*, colourless, shining rods, m. p. 120°. Lead tri-*p*-2-xylyl is remarkably stable towards air, and is not oxidised either in the solid state or in solution, although in the latter condition it is rapidly and completely decomposed on exposure to light. It is not sensitive to rise of temperature, and decomposition does not occur until 220°; for this reason, attempts to obtain *lead tetra*-p-2-*xylyl* by the action of magnesium *p*-2-xylyl bromide on lead chloride at elevated temperatures were unsuccessful, but the compound was readily prepared from lead tri-*p*-2-xylyl bromide and the Grignard reagent; it forms colourless, rectangular plates, m. p. 255°, which decompose above 270°, with separation of lead.

H. W.

Mixed Lead and Tin Aryls and Aryl Alkyls and their Application to the Synthesis of Organo-compounds of Silver. Examples of the Influence of Symmetry on the Properties of Chemical Compounds. ERICH KRAUSE and MARIA SCHMITZ (*Ber.*, 1919, **52**, [*B*], 2150—2164).—The conversion of the readily accessible lead aryl monohaloids and tin aryl monohaloids (A., 1918, i, 415) into mixed aryl and aryl alkyl compounds is described. Asymmetry in the latter appears to impart to the compounds lower m. p. and greater solubility and chemical activity, which is explained by the assumption that the metallic atom is more completely protected from contact with a reagent by the symmetrical union with, for example, four phenyl groups, whilst with unlike groups spaces are left, through which the reagent can penetrate. The lead and tin aryls or aryl alkyls react with a cold alcoholic solution of silver nitrate, yielding bright yellow precipitates, which could not always be isolated in a pure condition, but which are shown in the cases of lead and tin triphenylethyls to have the composition $2PhAg,AgNO_3$.

Mixed Lead Aryls and Aryl Alkyls.—The compounds are prepared by the addition of lead triphenyl bromide to an ethereal solution of the magnesium aryl bromide, and are isolated in the usual manner. Unnecessarily protracted heating and long exposure of the crude products or their solutions to light and the air of the laboratory are to be avoided. The yields are almost quantitative. The following substances are described: ***lead triphenyl* p-*tolyl***, hair-like needles, m. p. 125·5°; ***lead triphenyl* p-2-*xylyl***, transparent crystals, m. p. 104·5°; ***lead triphenyl* m-4-*xylyl***, rods arranged in clusters, m. p. 111·5—112°; ***lead triphenyl* p-*phenetyl***, small, shining needles, m. p. 119—120°; ***lead triphenyl α-naphthyl***, colourless needles grouped in rosettes, m. p. 101°; ***lead triphenyl*** cyclo-

hexyl, m. p. 119°; *lead triphenyl ethyl*, needles, m. p. 42°, $n_{H\alpha}^{61}$ 1·62628, D_4^{61} (vac.) 1·5885; *lead diphenyl di-α-naphthyl* (from lead diphenyl dibromide and magnesium α-naphthyl bromide), microscopic prisms, m. p. 197°; *lead di-α-naphthyl diethyl*, intergrown prisms, m. p. 116°.

Mixed Tin Aryls and Aryl Alkyls.—These are prepared from tin triphenyl chloride and excess of magnesium aryl or alkyl haloid in almost quantitative yield. The following substances are described: *tin triphenyl* p-*tolyl*, small, slender needles, m. p. 124°; *tin triphenyl* p-2-*xylyl*, coarse, six-sided plates, m. p. 100·5°; *tin triphenyl α-naphthyl*, colourless prisms, m. p. 125°; *tin triphenyl methyl*, large, shining rhombs, m. p. 60°, $D_4^{63\cdot85}$ (vac.) 1·3113, $n_{H\alpha}^{63\cdot85}$ 1·6001, $n_D^{63\cdot85}$ 1·60661, $n_{H\beta}^{63\cdot85}$ 1·62351, $n_{H\gamma}^{63\cdot85}$ 1·63831; *tin triphenyl ethyl*, ice-like crystals, m. p. 56°, D_4^{62} (vac.) 1·2953, $n_{H\alpha}^{62}$ 1·59917, n_D^{62} 1·60542, $n_{H\beta}^{62}$ 1·62236; tin tetra-*o*-tolyl (by action of a large excess of magnesium *o*-tolyl bromide on a suspension of the etherate of stannic chloride), white, crystalline powder, m. p. 158—159°.

Action of Mixed Lead and Tin Aryls on Silver Nitrate and Mercuric Chloride.—*Silver phenyl silver nitrate*, $2PhAg,AgNO_3$, is prepared by the cautious addition of a solution of lead triphenyl ethyl in absolute alcohol to an alcoholic solution of silver nitrate. It forms a canary-yellow, amorphous powder resembling cadmium sulphide in shade. The colour deepens rapidly when the substance is heated until decomposition occurs at about 100°, the exact temperature depending both on the rate of heating and on the age of the preparation. It explodes when heated in a test-tube. The colour is practically unchanged after twelve hours in complete darkness, but darkens within a few minutes on exposure to diffused light. Similarly, lead tripheuyl ethyl and mercuric chloride yield mercury phenyl chloride, leaflets, m. p. 250°. Tin triphenyl ethyl gives silver phenyl silver nitrate and mercury phenyl chloride with silver nitrate and mercuric chloride respectively, the products being identical with those prepared from the lead compound. Lead triphenyl *p*-phenetyl and silver nitrate yield a *product* which closely resembles the silver compound described above, but does not appear to be homogeneous. Lead tetraphenyl, tetra-*p*-tolyl, and tetra-*p*-2-xylyl are not acted on by cold alcoholic silver nitrate solution, but the solid compounds become grey, owing to the gradual reduction of the silver nitrate on protracted boiling of the solution. Lead triphenyl *p*-tolyl, triphenyl *p*-2-xylyl, and triphenyl *m*-4-xylyl have no action in dilute solution, or only cause a yellow coloration; with excess of concentrated silver nitrate solution, immediate precipitates closely resembling silver phenyl silver nitrate are formed, which give a colourless solution in the boiling solvent, and then yield a silver mirror and a brownish-yellow precipitate. Lead triphenyl α-naphthyl, diethyl dinaphthyl, and triphenyl *cyclo*hexyl yield immediate precipitates, even in dilute solution, which are very similar to one another in appearance and reactions, except in colour of the naphthyl componnds, which is orange-yellow; the latter substances yield naphthalene when treated with hydrochloric acid.

Lead diphenyl di-α-naphthyl does not react with alcoholic silver nitrate.

The aromatic tin compounds react less readily than the corresponding lead compounds. Tin tetraphenyl does not react; tin *triphenyl p-tolyl* and *triphenyl p-2-xylyl do not act in cold* solution, and cause reduction when boiled. Tin triphenyl phenetyl gives a yellow precipitate after a few seconds, whilst tin triphenyl methyl, like the ethyl compound, gives an immediate precipitate of silver phenyl silver nitrate, which becomes black when warmed.

According to the literature, the lead alkyls immediately reduce silver nitrate; the authors' hypothesis, that very unstable silver alkyls are formed as intermediate products, is confirmed by the observation that yellow precipitates are formed, which are stable at $-30°$ for several seconds, and at $-80°$ for several minutes.

H. W.

Physiological Chemistry.

Analyses of Blood Gases. III. The Permeability of Human Erythrocytes to Chlorions. H. Straub and Klothilde Meier (*Biochem. Zeitsch.*, 1919, **98**, 205—228. Compare A., 1919, i, 53).—Blood corpuscles suspended in a physiological sodium chloride solution were subjected to the influence of various concentrations of carbon dioxide. It was found that the corpuscles acted as "buffers" towards carbon dioxide. The hydrion concentration of the inside of the cells exceeded $P_H = 7·00$ only when the sodium chloride solution in which the corpuscles were suspended reached an hydrion concentration of $P_H = 6·67$. This is, no doubt, brought about by the alteration in the colloidal condition of the cell membrane. The change in the hydrion concentration was found to be independent of the concentration of Cl and Na ions of the solution in which the corpuscles are suspended as long as a certain minimum of these ions was assured and the solntion made isotonic. In hypertonic 0·2 molar salt solutions, the change in the corpuscles was brought abont at the same hydrion concentration, namely, $P_H = 6·67$. In a hypertonic 0·102 molar solution, on the other hand, the change took place earlier.

S. S. Z.

Analyses of Blood Gases. IV. The Influence of Alkali Ions on the Hæmoglobin and Cell Membrane. H. Straub and Klothilde Meier (*Biochem. Zeitsch.*, 1919, **98**, 228—256).—The influence of alkali ions on the electrical charge of hæmoglobin and on the permeability of the membrane of human erythrocytes to these ions has been studied. The membrane becomes permeable to the various ions at the following hydrion concentrations: Li and Na at $P_H = 6·67$, K at $P_H = 6·8$, Rb at $P_H = 6·92$, Cs at $P_H = 7·06$. The hæmoglobin loses its charge on the addition of the alkali ions

at the following hydrion concentrations: Na and K at $P_H = 7 \cdot 00$, Rb at $P_H = 7 \cdot 22$, Cs at $P_H = 7 \cdot 34$. The membrane becomes permeable to ammonium ions in low concentrations at $P_H = 7 \cdot 48$. Higher concentrations of these ions require a higher hydrion concentration before the membrane becomes permeable to them. The action of ammonium ions on the charge of the hæmoglobin is similarly influenced by the concentration of the ions. The analogy between the permeability of the cell membrane to the alkali ions, and the precipitation of colloids by means of these ions, is pointed out. The bearing of the adsorption theory on the permeability of the cell membranes to alkali ions is also discussed. S. S. Z.

Influence of High Temperatures and Dilute Alkalis on the Antineuritic Properties of Food. AMY L. DANIELS and NELLIE I. MCCLURG (*J. Biol. Chem.*, 1919, **37**, 201—213).—The results obtained by these authors are not in accord with those reported by McCollum and Simmonds (*ibid.*, 1918, **33**, 55). It appears improbable that the commercial canning of foods is responsible for a serious destruction of the antineuritic vitamine, and the warning sounded by Chick and Huma (*Proc. Roy. Soc.*, 1917, [*B*], **90**, 60) is regarded as unfounded. J. C. D.

The Vitamines of Green Foods. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (with co-operation of EDNA L. FERRY and ALFRED J. WAKEMAN) (*J. Biol. Chem.*, 1919, **37**, 187—200).—Dried yeast is somewhat more than four times as efficient as dried spinach leaves when used as a source of the water-soluble vitamine. These leaves, however, appear to be a rich source of fat-soluble *A*. The values of cabbage, lucerne, clover, and timothy plants in supplying the water-soluble accessory substance are of the same order as that of spinach, but the experiments are not regarded as complete.

Very small amounts of lucerne, clover, and timothy plants will supply sufficient fat-soluble *A* for the growth of young rats. Emphasis is therefore laid on the importance of fresh green vegetables in the human dietary. J. C. D.

Identity of the Water-soluble Growth-promoting Vitamines and the Antineuritic Vitamine. H. H. MITCHELL (*J. Biol. Chem.*, 1919, **40**, 399—413).—The author reviews the literature dealing with the distribution, properties, and character of these two substances, and forms the opinion that there is as yet insufficient evidence to assume that they are identical. J. C. D.

Formation of Urea by the Placenta. FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1919, **37**, 105—112).—Formation of urea by the placenta may be conclusively demonstrated, although the processes leading up to its production can only be surmised.

J. C. D.

Physical Properties and Chemical Composition of Human Amniotic Fluid. DOKO UYENO (*J. Biol. Chem.*, 1919, **37**, 77—101).—The human amniotic fluid at the end of pregnancy

always contains coagulable albumins (an average of 0·226%, inclusive of mucin). The quantity of mucin was too small to be estimated. Peptones and proteoses were not found. Approximately 0·003% of ammonia and 0·0323% of urea were found, together with very small amounts of uric acid and creatine, but creatinine and hippuric acid were absent. Cholesterol is also a component of the human amniotic fluid. J. C. D.

The Effect of Pyretics and Antipyretics on Catalase Production. W. E. BURGE (*J. Pharm. expt. Ther.*, 1919, **14**, 121—130).—Tetrahydro-β-naphthylamine, adrenaline, caffeine, and sodium chloride stimulate the alimentary glands, particularly the liver, to an increased output of catalase; this fact is offered in explanation of the increased oxidation produced by these substances, and hence of the accompanying fever, in so far as the increased heat production is involved in this. Chloroform decreases catalase both by decreasing its output from the liver and by direct destruction of this enzyme. Ether decreases catalase principally by direct destruction of the enzyme without disturbing the liver function so much as does chloroform. Acetanilide, quinine, and phenacetin produce a slight decrease in catalase by decreasing its output from the liver. Chloroform and ether lower temperature in so far as decreased oxidation is involved in this by decreasing catalase the enzyme principally responsible for oxidation in the body. The fact that acetanilide, quinine, and phenacetin have little or no effect in decreasing catalase suggests that their mode of action in lowering temperature is not due to a decrease in oxidation. J. C. D.

The Carnosine Content of Normal and Pathological Human Cardiac Muscles. F. BUBANOVIĆ (*Biochem. Zeitsch.*, 1918, **92**, 125—129).—The carnosine content of the human heart is very constant, and is not influenced either by hypertrophy or atrophy of the muscles. The average content is 0·25%. The carnosine was determined when possible, both by the diazo and the copper colorimetric methods. S. S. Z.

Bioluminescence. X. Production of Carbon Dioxide during Luminescence of Cypridina Luciferin. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, **2**, 133—135).—All luminous animals require oxygen for luminescence, but there has previously been some doubt as to whether carbon dioxide is given off as a result of this phenomenon. A brilliant luminescence results when a small amount of luciferase solution is added to a solution of *Cypridina* luciferin (A., 1919, i, 299), so that it should be possible to ascertain whether this process is accompanied by a liberation of carbon dioxide. The results of experiments indicate that the oxidation of luciferin which is responsible for luminescence is not to be compared with the reactions in cells giving rise to the carbon dioxide of respiration. As previously suggested by the author, the process is probably similar to the oxidation of a leuco-dye (A., 1919, i, 299). J. C. D.

Bioluminescence. XI. Heat Production during Luminescence of Cypridina Luciferin. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, **2**, 137—143).—The heat change during the oxidation of luciferin by luciferase was investigated in order to ascertain the nature of the luminescent reaction. The change observed was so small that it is estimated that 1 gram of luciferin develops less than 0·1 cal. during the oxidation process accompanying luminescence. This clearly differentiates this type of reaction from those such as the oxidation of dextrose, 1 gram of which will give 4000 cal. It therefore appears probable that no carbon dioxide is produced during the oxidation of luciferin, and that the process is one more closely resembling the oxidation of leucomethylene-blue (compare preceding abstract). J. C. D.

Physiology of Phosphorus and Calcium Metabolism as Related to Milk Secretion. EDWARD B. MEIGS, N. R. BLATHERWICK, and C. A. CARY (*J. Biol. Chem.*, 1919, **37**, 1—75). —Normal blood plasma contains no phosphorised protein, and probably no phosphorus compounds other than phosphatides and inorganic phosphates. The phosphorus of these two classes of compounds certainly comprises more than 97% of all that exists in normal plasma. The precursor in plasma of milk fat and milk phosphorus is of a phosphatide nature. The concentration of calcium in the plasma of cows is quite constant. Small variations can be induced by varying the amount supplied with the rations, but the chief controlling factor is probably the concentration of bicarbonate in the plasma. It is probable that the concentration of calcium tends to vary inversely with that of the bicarbonate. The concentrations of phosphatide and inorganic phosphates in the plasma are highly variable. Both can be made to vary by changing the amount of phosphorus supplied with the rations, though the variations induced in this manner show themselves most markedly in the inorganic phosphate. Both undergo variations as the accompaniment of increasing age and of the later stages of pregnancy. The phosphatide of the plasma shows a marked tendency to rise during the first month of lactation, and to remain high until lactation has ceased. This phenomenon is largely independent of the diet, and is thought to be connected with the fact that near the beginning of lactation there is a tendency for the body fat to be released from its stores and thrown out into the blood.

J. C. D.

Pyrrole and Melanuria. PIETRO SACCARDI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 85—89).—Administration of pyrrole leads to the formation of melanin in the urine in the case of the rabbit, but not in that of the dog; the latter, being essentially a carnivorous animal, appears easily to oxidise those products of the scission of proteins which lead to the formation of pyrrole, whereas with herbivorous animals the oxidation proceeds only as far as melanogen. Melanins have been obtained from rabbits' urine, from cuttle-fish, from black hair, from the choroid, and from a melanotic tumour,

the properties and reactions of the different products being described. These melanines all resemble closely pyrrole-black obtained by the chemical oxidation of pyrrole; when heated in a test-tube, they yield crystalline sublimates in the form of black, orthorhombic lamellæ, whereas precipitation of the melanines gives amorphous masses.

The glandular oxidation of pyrrole in aqueous suspension containing a few drops of toluene has been studied in vitro at about 40°, the glands used being the mamma, liver, testicles, thyroid, kidneys, and spleen of the ox. The glandular tissue gradually turns brown, and assumes the appearance of an ordinary melanotic tumour; the most intense blackening is shown by the liver and spleen, the testicles, kidneys, and thyroid following in order. The mamma exhibits no blackening after six days, and even undergoes putrefaction, in spite of the presence of toluene. Addition of adrenaline accelerates the blackening of the glandular organs.

T. H. P.

The Physical Theory of the Action of Drugs and Poisons. I. TRAUBE (*Biochem. Zeitsch.*, 1919, **98**, 177—197).—A theoretical paper. The pharmacological action of drugs and toxins is attributed mainly to their physical properties. It is urged that more attention ought to be given to the physical side of these principles in the study of chemotherapy. S. S. Z.

The Biological and Pharmacological Properties of Chlorophyll. EMIL BÜRGI and C. F. VON TRACZEWSKI [with (FRL.) SCHEINA BASS, A. BRAUNSTEIN, and (FRL.) S. FRIDKISS] (*Biochem. Zeitsch.*, 1919, **98**, 256—284).—The hæmoglobin-forming capacity of chlorophyll was studied in a series of experiments in which the latter was administered to rabbits made anæmic by means of bleeding and by the action of phenylhydrazine. It was found that chlorophyll, as well as iron, when given in large doses possessed a blood-forming capacity. Both chlorophyll and iron were equally effective, whether the experimental anæmia was induced by bleeding or by the administration of phenylhydrazine. Small doses of chlorophyll were fouud to possess a "sensitising" effect on the action of iron in the production of blood. S. S. Z.

Blood-forming Properties of Chlorophyll. R. GRIGORIEW (*Biochem. Zeitsch.*, 1919, **98**, 284—294).—Chlorophyll in the form of phæophytin possesses a higher blood-forming capacity than iron when given to normal or naturally anæmic rabbits. The best results are achieved with these auimals by the administration of a combination of iron and chlorophyll. S. S. Z.

Maximum Production of Glutamine by the Human Body as Measured by the Output of Phenylacetylglutamine. CARL P. SHERWIN, MAX WOLF, and WILLIAM WOLF (*J. Biol. Chem.*, 1919, **37**, 113—119).—No marked increase in sulphur metabolism

followed the ingestion of phenylacetic acid by man. This does not agree with the experimental results of E. and H. Salkowski working with rabbits (A., 1879. 662). Intestinal putrefaction, as measured by the excretion of ethereal sulphates, is decreased after administration of phenylacetic acid. About half of the acid administered was excreted in combination with glutamine.

J. C. D.

Comparative Metabolism of certain Aromatic Acids. III. Fate of *p*-Nitrophenylacetic Acid in the Organism of Fowl, Dog, and Man. CARL P. SHERWIN and MAX HELFAND (*J. Biol. Chem.*, 1919, **40**, 17—27).—The human organism eliminated 68·7% of the ingested *p*-nitrophenylacetic acid in the urine in the unchanged condition. Attention is drawn to the peculiar fact that this acid, although toxic to the body, is excreted without having been rendered innocuous by combination with some substance, such as glycine, in its passage through the tissues. When administered to the dog, the greater part is excreted unchanged, but some is found to be present in the urine as *p*-nitrophenylaceturic acid. In the case of the fowl, a certain amount of the *p*-nitrophenylacetic acid is excreted unchanged, but the greater part is combined with ornithine in the body and excreted as *p-nitrophenylacetylornithinic acid*, $C_{21}H_{22}O_8N_4$, short, thick, irregular needles, m. p. 184—185°.

J. C. D.

Behaviour of Sudan III in the Animal Organism. B. E. READ (*J. Biol. Chem.*, 1919, **37**, 121—135).—Sudan III dissolved in oil and administered intraperitoneally, subcutaneously, or by the mouth is absorbed, and may be traced in the lymph, blood, and bile. It is transported to the fatty tissue of the body, being deposited particularly in the omentum. It is excreted in the fæces, and is not found in the urine of normal animals. Ordinary commercial preparations of Sudan III contain more or less impurity of a toxic nature. The foreign substances are excreted in the urine, which is deeply coloured, and may cause death. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

The Catalase of Bacteria. II. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **92**, 129—139. Compare A., 1918, i, 517).—The bacterial catalase obtained by the author obeys the same reaction laws as catalases already studied. S. S. Z.

Acidity Relationships of True Lactic Acid Bacteria. OLOF SVANBERG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 2, 1—10).—The author has investigated the acidity conditions

under which various micro-organisms can ferment milk and under which they can continue to grow. The change in the acidity of milk and whey by *Streptococcus lactis* has been ascertained at 16° and 37°, both by titration with $N/10$-sodium hydroxide and by Sörensen's method. At 16°, the P_H value in both cases is the same, 4·0, but the titration values are very different. *Bacterium casei* ε, in milk and wort at 35° raises the acidity to $P_H = 3·05$. If a pure *S. lactis* culture is placed in milk and allowed to act until the maximum acidity is reached, and the acidity is neutralised by alkali, the coccus will again produce acid, but the final concentration will be less than before, and this will be continued if the process of alternate fermentation and neutralisation is continued. The final acidity value is reduced by the addition of sodium lactate to milk proportionally to the lactate concentration. The acid tolerance of *S. lactis* is determined for sulphuric acid, hydrochloric acid, and phosphoric acid, and the same value found in each case, namely, $P_H = 3·4$ at 18°; in the case of *B. casei* ε, the acid tolerance is found to be $P_H = 3·0$ at 35° for hydrochloric acid and phosphoric acid. The alkali tolerance of *S. lactis* at 18° lies at $P_H = 8$. J. F. S.

The Surface Action of the Homologues of Hydroquinine and their Toxins. I. Traube (*Biochem. Zeitsch.*, 1919, **98**, 197—205).—The hydrocupreines and their homologues show a parallelism between their disinfecting power against many bacilli and cocci, mostly gram-positive organisms, and their surface action. An analogy also exists between the susceptibility of bacteria towards basic stains and their power of adsorption of hydrocupreines and their toxins. S. S. Z.

Gentian-violet, its Selective Bactericidal Action. M. L. Crossley (*J. Amer. Chem. Soc.*, 1919, **41**, 2083—2090).—Gentian-violet is a mixture of dextrin and dye in almost equal proportions, the dye being a mixture consisting chiefly of hexamethylpararosaniline hydrochloride and pentamethylpararosaniline hydrochloride with small amounts of the tetramethyl compound and lower homologues.

The selective bactericidal action of gentian-violet is no greater than that of its component dyes, and gentian-violet has no advantage over these in selective or differentiating power. Organisms which were gentian-positive were also gram-positive, the structure of the dye and of the organism being important factors in the selective action. The concentration of the dye is an important factor in determining its power to kill an organism. Not one of the dyes examined was effective for *B. subtilis* in dilutions greater than 1 in 100,000. *B. mycoides* was, however, killed by malachite green in dilution of 1 in 100,000, by rosaniline in dilution of 1 in 200,000, and by gentian-violet, or either of its two principal components, in dilution of 1 in 300,000. The basic nitrogen groups appear to be the reactive groups, and their action is intensified by substitution of methyl for amino-hydrogen. W. G.

The Influence of Potassium Salts on the Enzyme of Aspergillus Oryzæ which Liquefies Starch. GEN-ITSU KITA (*Mem. Coll. Eng. Kyoto*, 1918, **2**, 1).—Potassium salts promote the property of the enzyme to liquefy starch even when the saccharification is retarded. On the addition of suitable quantities of these salts to the mash no blue coloration is obtained with iodine after the fermented wort is boiled. This reaction, according to the author, is usually present when these salts are not added. The above facts are of technical significance. S. S. Z.

Formation of Acids by Moulds and Yeasts. II. FRIEDRICH BOAS and HANS LEBERLE (*Biochem. Zeitsch.*, 1918, **92**, 170—188. Compare A., 1919, i, 508).—The formation of acids by *Mycoderma*, *Oidium*, and *Aspergillus niger* in media containing various carbohydrates and nitrogenous ingredients has been studied. The greater part of the acid is formed from the carbohydrate. When, however, an ammonium salt of a strong acid forms the source of nitrogen, the liberated acid suppresses the formation of acid from the carbohydrate. The ammonia formed in the fermentation process from the various nitrogenous compounds by means of enzymic action greatly influences the formation of acid. This is dependent on the character of the organism and the nature of the carbohydrate employed. S. S. Z.

Natural and Artificial Formation of Glycerol in Alcoholic Fermentation. CARL NEUBERG and ELSA REINFURTH (*Biochem. Zeitsch.*, 1918, **92**, 234—267).—By employing sodium sulphite as "fixing" agent for the acetaldehyde formed in alcoholic fermentation an equivalent amount of glycerol is also formed. More than 70% of the theoretical amount of acetaldehyde is thus fixed. The amount of acetaldehyde and glycerol produced increases with the amount of sulphite employed. Acetaldehyde and glycerol are therefore not only by-products, but are produced in considerable quantities in certain stages of alcoholic fermentation. S. S. Z.

Autolysis of Yeast in its Dependence on Hydrogen and Hydroxyl-ions. K. G. DERNBY (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 23, 1—26).—On the basis that enzymes are amphoteric electrolytes, the author has examined the autolysis of yeast at various temperatures in the presence of electrolytes. It is shown that the simple yeast cell contains enzymes which are capable of degrading albuminons substances. These enzymes are analogous in type with those present in specific animal organs. The enzymes identified in the paper are (*a*) yeast pepsin, which degrades albuminous substances to peptones, and has a maximnm activity at $P_H=4$—$4{\cdot}5$, (*b*) yeast tryptase, which does not attack the yeast alhumin, but destroys gelatin, casein, Witte-peptone, and similar substances, and has a maximum activity at $P_H=7{\cdot}0$, (*c*) yeast eriptase, which degrades polypeptides to amino-acids and has a maximum activity at $P_H=7{\cdot}8$. The autolysis of yeast is brought about by these enzymes and consists in a successive degradation of

albumin; it can only proceed when the different enzymes can operate simultaneously. The best hydrogen-ion concentration for the process is $P_H = 6\cdot1$, which lies between that of yeast tryptase and yeast pepsin. J. F. S.

Extraction and Concentration of the Water-soluble Vitamine from Brewer's Yeast. THOMAS B. OSBORNE and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1919, **40**, 383—394).—By precipitation of a dilute acetic acid extract of yeast with alcohol the authors have succeeded in obtaining a fraction which appears to contain a very large proportion of the water-soluble accessory substance present in the original yeast. The chemical nature of the substances in this fraction is not yet determined. J. C. D.

Examination of the Urease-content of Indigenous Seeds. D. H. WESTER (*Chem. Weekblad*, 1919, **16**, 1548—1551).—The urease content of a large number of seeds was determined. It varied from nil or very small amounts up to a considerable quantity in the laburnum. Plants of the same natural order differ widely in regard to the urease content of their seeds. In no case did the amount of urease approach that found in soja beans or canavalia beans, and of these the latter contained approximately ten times as much urease as the former. W. J. W.

Do Seedlings Reduce Nitrates? J. DAVIDSON (*J. Biol. Chem.*, 1919, **37**, 143—148).—The author reaches the conclusion that growing seedlings do not, as part of their metabolic processes, reduce the nitrates in the outside medium in which they are growing. J. C. D.

Complex Iron Salts. I. OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1918, **92**, 189—198).—In mixed aqueous solutions of ferric chloride and formaldoxime, phloroglucinol, catechol, or resorcinol exposed to the air, tervalent iron is slowly reduced to its bivalent form in the presence of dilute hydrochloric acid. Similarly, in admixed solutions of ferric chloride and quinol, acetylacetone, acetoacetic ester, salicylaldehyde, salicylic acid, and catechol-*o*-carboxylic acid, the above reduction is only effected after exposure to the rays of a mercury quartz lamp or sunlight. Aqueous solutions of ferric chloride and dimethylglyoxime, on the other hand, are not reduced even after exposure to the light. The chemistry of these observations and their bearing on some physiological phenomena of the plant are discussed. S. S. Z.

Presence in Plants of Hæmatoid Iron Compounds. III. G. GOLA (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii. 146—150).—Experiment indicates that the peroxydasic function in plants is due in most cases, not only to true enzymes, but also to various iron compounds. The latter are probably catabolic products of more complex compounds, such as the hæmatoids, which largely form crustations on the cellular membranes, and are, in virtue of their

physical state, able to act between the oxidisable substances and the peroxides. T. H. P.

Position and Osmotic Pressure. O. Arrhenius (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 15, 1—20).—A discussion of the relation between the osmotic pressure of the cell sap and the position of plants and trees. By "position" is meant, not only the geographical position, but also the factors, such as light, heat, moisture, winds, composition of the substratum, etc., which affect the growth of the plants. T. S. P.

The Isoelectric Points of the Proteins in certain Vegetable Juices. Edwin J. Cohn, Joseph Gross, and Omer C. Johnson (*J. Gen. Physiol.*, 1919, **2**, 145—160).—The hydrogen-ion concentration of filtered potato juice is approximately $10^{-7}N$. The isoelectric point of tuberin, the chief protein of the potato, determined by the cataphoresis method, is at a hydrogen-ion concentration slightly lower than $10^{-4}N$. At acidities greater than the isoelectric point, tuberin exists combined with acid. The isoelectric point of the protein in carrot juice coincided with that of tuberin, and the properties of carrot juice and potato juice were found to be remarkably similar.

The protein of the tomato existed in a precipitated form near its isoelectric point. Accordingly, it was not present to any extent in filtered tomato juice. If, however, the considerable acidity of the juice was neutralised, the protein dissolved and was filterable. The addition of sufficient acid to make the hydrogen-ion concentration slightly greater than $10^{-5}N$ again precipitated the protein at its isoelectric point. J. C. D.

Fat-soluble Vitamine. II. The Fat-soluble Vitamine Content of Roots, together with some Observations on their Water-soluble Vitamine Content. H. Steenbock and E. G. Gross [with M. T. Sell] (*J. Biol. Chem.*, 1919, **40**, 501—531).—In the plant kingdom, the occurrence of the fat-soluble vitamine cannot always be associated with a preponderance of actively functionating cells, as distinguished from those that serve primarily as storage organs. Thus the sweet potato is rich in this accessory factor, whilst the ordinary potato contains very little; similarly, in the case of the roots, carrots contain much of the vitamine, but beets and mangels do not.

In the case of the water-soluble vitamines, the carrot, rutabaga, and dasheen contain more than do sugar-beets and mangels.

J. C. D.

Reducing Action of Roots of the Gramineæ: Reduction of Calcium Nitrate. I. and II. Giovanni Sani (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 199—201, 244—247).—When the roots of wheat, maize, and oats, gathered at the beginning of the flowering period, are pounded in a mortar and then extracted with boiling water, liquids are obtained which exert pronounced reducing action

on *Fehling's* solution. The pulped roots, which have an acid reaction, are also able, in the cold, to reduce calcium nitrate, this reduction being inhibited by the presence of alkaline Rochelle salt solution. The reduction of calcium nitrate proceeds only to a definite limit, and then ceases entirely, the product of the reduction apparently acting as a poison towards the reducing agent; in the plant itself, however, such poisoning action would not occur, utilisation of the reduction product preventing its accumulation. The nature of this reduction product has not yet been established.

T. H. P.

Globulin of the Coconut, Cocos nucifera. I. Preparation of Coconut Globulin. Distribution of the Basic Nitrogen in Coconut Globulin. CARL O. JOHNS, A. J. FINKS, and C. E. F. GERSDORF (*J. Biol. Chem.*, 1919, **37**, 149—153).—The globulin contains the following amounts of basic amino-acids: cystine, 1·44%; arginine, 15·92%; histidine, 2·42%; lysine, 5·80%. Tryptophan is present. The free amino-nitrogen was found to equal nearly one-half of the lysine nitrogen. J. C. D.

Globulins of the Jack Bean, Canavalia ensiformis. JAMES B. SUMNER (*J. Biol. Chem.*, 1919, **37**, 137—142).—Two crystalline globulins and one non-crystalline globulin have been isolated from the jack bean. *Concanavalin B* crystallises in needles, slowly soluble in 10% sodium chloride, soluble in excess of alkali; *concanavalin A* crystallises in bisphenoid form, insoluble in any but concentrated salt solutions; canavalin, the uncrystallisable globulin, is readily soluble in 1% sodium chloride solution (compare Jones and Johns, A., 1917, i, 191). J. C. D.

Examination of the Urease-content of Soja Beans from Various Sources. D. H. WESTER (*Chem. Weekblad*, 1919, **16**, 1552—1556).—Nearly all the varieties examined showed a high urease content, and this was not diminished by age. The lowest enzymic action was found in soja beans from the Cameroons and Germany, which raises an interesting question in regard to diminution of effectiveness bronght about by transferring the plant from its original habitat, Asia. W. J. W.

A Quantitative Relation between Soil and the Soil Solution brought out by Freezing-point Determinations. BERNARD A. KEEN (*J. Agric. Sci.*, 1919, **9**, 400—415).—Bouyoucos and his co-workers, by determinations *in situ* of the freezing-point depression of soil solution, at varying moisture contents, have shown that the soil solution in quartz sand and extreme types of sandy soil obeys approximately the same law as dilute solutions, but that the soil solutions of ordinary soils do not obey this law (compare *J. Agric. Sci.*, 1914, **6**, 456). Bouyoucos assumes that some of the soil water is rendered unfree in the sense that it does not take part in the depression of the freezing point. The present author, accept-

ing the truth of this assumption, and using some of Bouyoucos's data, has shown that the water rendered unfree is not a constant amount, but varies with the total moisture content. A definite relation exists between the free, unfree, and total moisture expressed by the equations $Y_n = cM_n^x$ and $Z_n = Y_n^{1/x}/c^{1/x} - Y_n$, where c and x are constants for any one soil, and M_n, Y_n, and Z_n represent respectively the total, free, and unfree water. Over the experimental range the ratio of free to total water continually decreases, and that of unfree to total water continually increases as the total moisture diminishes in amount. The constant c contains an unknown factor, namely, the quantity of free water at the highest amount of total water used in the experiments, and according to the value arbitrarily assigned to it so the amount of unfree water may continually decrease with decrease of total moisture over the experimental range or may increase to a maximum and then decrease. The same general conclusions on the relations existing between the soil and its moisture constant as were drawn from the author's experiments (compare *loc. cit.*) on the evaporation of water from soil, again follow. W. G.

Soil Acidity, the Resultant of Chemical Phenomena. H. A. Noyes (*J. Ind. Eng. Chem.*, 1919, **11**, 1040—1049).—Chemical reactions are held to be the cause of soil acidity. The presence of free hydrogen ions in the soil extract is considered to be due to hydrolysis. As regards the action of organic matter, physicochemical explanations of the hydrolysis of silicates and of organic matter and the ability of organic matter to form complex ions with bases are more satisfactory than are "adsorption" theories. The reaction of a soil at any time depends on the nature of its constituents and the proportions in which they are present with water. Change in the water content, removal of substances from solution, and the addition of other substances, all alter the reaction of the soil in accord with the law of mass action. W. P. S.

The Richness in Copper of Cultivated Soils. L. Maquenne and E. Demoussy (*Compt. rend.*, 1919, **169**, 937—942).—The authors have not estimated the total copper, but the amount which is dissolved when 6 grams of the soil are boiled very gently for half an hour with 50 c.c. of 10% sulphuric acid. Arable soils contain very little copper, the amount varying, in the soils examined, from 1 to 50 mg. per kilogram of soil, but in the case where the high figure was obtained the soil had carried crops which had frequently been treated with copper sulphate. In the case of vineyard soils, where it was known that the vines had been treated with copper sulphate over a long period of years, the copper content rose to as high as 250 mg. per kilo. of soil. The copper was almost entirely found in the surface layer of the soil, the penetration being extremely slow. Despite the high copper content of some of these soils, there was no indication of any toxic effect on the vines.

W. G.

The Amount and Composition of Rain Falling at Rothamsted (Based on Analyses made by the late Norman H. J. Miller). E. J. Russell and E. H. Richards (*J. Agric. Sci.*, 1919, **9**, 309—337).—A summary of the results of analyses of Rothamsted rain water made by the late N. H. J. Miller from 1888 to 1916. The rain water contained, on an average, 0·405 part per million of ammoniacal nitrogen, 0·204 part per million of nitric nitrogen, 2·43 parts per million of chlorine, and 10 parts per million of dissolved oxygen. Both the yearly and monthly fluctuations of ammoniacal nitrogen move in the same direction as the rainfall, the general level being highest in May, June, July, and August, and lowest in January, February, March, and April. Up to 1910 the nitric nitrogen fluctuated in amount year by year and month by month in the same way as the ammoniacal nitrogen, but since that date there has been no simple relationship. The fluctuations of the chlorine content of the rain closely follow the rainfall, but the general level is much higher during the months September to April than during the summer months.

The sources of ammonia in the rain are given as the sea, the soil, and city pollution; the soil is indicated as an important source by the fact that the ammonia content is high during periods of high biochemical activity in the soil, and low during periods of low biochemical activity. Further, the close relationship between the amounts of ammoniacal and nitric nitrogen suggests either a common origin or the production of nitric compounds from ammonia. It seems probable that the chlorine comes from the sea, but some may come from fuel.

During the period under examination there has been a rise in the amounts of nitric nitrogen and of chlorine in the rain, and a tendency for the ammonia content to drop. It is suggested, as a possible explanation, that some former source of ammonia is now producing nitric nitrogen; it is possible that modern gas-burners and grates tend to the formation of oxides of nitrogen rather than ammonia.

There is a marked difference in composition between summer and winter rain water, which suggests that these may differ in origin. The winter rain resembles Atlantic rain in its high chlorine and low ammonia and nitrate content; the summer rain is characterised by low chlorine but high ammonia and nitrate content, and it is suggested that it may arise by evaporation of water from the soil and condensation at higher altitudes than in the case of winter rain.

W. G.

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Organic Chemistry.

Oxidation of Methane. R. K. BAILEY (U.S. Pat. 1319748).—Methane or natural gas is mixed with twice its volume of nitric oxide and with sufficient oxygen or air to form nitrogen peroxide. This mixture is passed through a porcelain or other inert tube heated to redness. Oxidation products, including formaldehyde, are obtained. The oxidation is prevented from being carried too far by conducting the reaction products as quickly as possible into a cooling chamber, where they are brought into contact with a sludge of calcium carbonate, which unites with the oxides of nitrogen, except nitric oxide. Formaldehyde is recovered from the solution after separating the solids from the sludge. Instead of using calcium carbonate, the hot reaction gases may be brought into contact with calcium oxide to effect absorption of water, thus preventing formation of nitrous and nitric acids, which if present would oxidise the formaldehyde. Reaction temperatures as low as 450° may be employed. CHEMICAL ABSTRACTS.

Methyl Sulphate. T. H. DURRANS (U.S. Pat. 1317648).—Methyl sulphate is produced, together with methyl hydrogen sulphate and methyl chloride, by treating methyl alcohol, preferably with cooling, with chlorine and sulphur dioxide, the latter preferably being in slight excess throughout the reaction. Methyl chloride is removed by distillation at the ordinary pressure and the methyl sulphate under reduced pressure, or the products may be used together as alkylating agents. CHEMICAL ABSTRACTS.

Improvements in the Manufacture of Aliphatic Nitrites. PAUL RENE DE WILDE (Brit. Pat. 133304).—Nitrites of aliphatic alcohols are produced by the reducing action of sulphur dioxide on solutions of the alcohols in pure or diluted nitric acid, or, alternatively, a saturated alcoholic solution of sulphur dioxide may be mixed with nitric acid. As an example, 74 grams of *iso*butyl alcohol dissolved in 100 grams of nitric acid (D 1·375) yield on treatment with sulphur dioxide 85 grams of *iso*butyl nitrite.
G. F. M.

Preparation of Chloromethyl Carbonates. ANDRÉ KLING, D. FLORENTIN, and E. JACOB (*Compt. rend.*, 1920, **170**, 111—113. Compare this vol., i, 139, and Grignard, Rivat, and Urbain, this vol., i, 139).—By the successive chlorination of methyl carbonate, mono-, di-, tri-, tetra-, penta-, and hexa-chloro-derivatives are obtained, the most symmetrical derivative being obtained in each case. W. G.

Properties of the Chloromethyl Carbonates. ANDRÉ KLING, D. FLORENTIN, and E. JACOB (*Compt. rend.*, 1920, **170**, 234—236).—The physical properties of the nine possible chlorinated

methyl carbonates, the preparations of which have previously been described (preceding abstract), are given, as below:

Formula.	M. p.	B. p./760 mm.	B. p./50 mm.	D^{15}.
$CH_2Cl·O·CO_2Me$ ...	—	139—140°	67°	1·303
$CO(O·CH_2Cl)_2$ ...	—	176°	99°	1·480
$CHCl_2·O·CO_2Me$ ...	—	147°	72°	1·421
$CHCl_2·O·CO_2·CH_2Cl$	—	178°	102°	1·562
$CCl_3·O·CO_2Me$ ...	−70° (viscous)	165°	86°	1·535
$CO(O·CHCl_2)_2$ ...	−40°	182—183°	105—106°	1·618
$CCl_3·O·CO_2·CH_2Cl$ ...	−70° (viscous)	150° (decomp.)	110°	1·631
$CCl_3·O·CO_2·CHCl_2$ ...	−30°	196° ,,	115°	1·686
$CO(O·CCl_3)_2$	78°	203° ,,	124°	—

The substances which contain the group $·O·CCl_3$ are particularly toxic. W. G.

Organic Derivatives of Tellurium. I. Dimethyltelluronium Dihaloids. RICHARD HENRY VERNON (T., 1920, **117**, 86—98).

The Industrial Chloromethyl Formates and their Analysis. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1920, [iv], **27**, 39—45).—The mono- and di-chloromethyl chloroformates are decomposed by dilute alkali according to the equations:

$$Cl·CO_2·CH_2Cl + H_2O = 2HCl + CO_2 + H·CHO,$$
$$Cl·CO_2·CHCl_2 + H_2O = 3HCl + CO_2 + CO.$$

The corresponding mono- and di-chloromethyl formates give

$$H·CO_2·CH_2Cl + H_2O = H·CO_2H + H·CHO + HCl,$$
$$H·CO_2·CHCl_2 + H_2O = 2HCl + 2CO + H_2O.$$

The formaldehyde formed may be estimated by Romijn's method (compare A., 1897, ii, 166), the formic acid by Pean de St. Gilles's method (compare *Ann. Chim. Phys.*, 1859, **55**, 374), and the carbon monoxide by direct measurement of its volume after decomposing the material with sodium hydroxide. These results, together with the percentage of chlorine, enable an idea to be formed as to the different esters present in industrial chlorinated methyl formates. [See, further, *J. Soc. Chem. Ind.*, 1920, 205A.] W. G.

Manufacture of Esters of Ethylenic Halogenhydrins. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 128911).—Ethylene halogenhydrin esters of the general formula

$$R·CO_2·CH_2·CH_2X,$$

where R is an alkyl or aryl group and X a halogen, are prepared by the interaction of ethylene oxide and an acidyl haloid in equimolecular proportions at a suitable temperature, depending on the particular acid chloride or bromide used. The reaction is conveniently brought about by passing gaseous ethylene oxide through the acidyl haloid at ordinary atmospheric pressure, and quantitative yields are obtained. Examples are given of the preparation of *β-chloroethyl acetate*, b. p. 143—144°, from acetyl chloride at its boiling point, *β-chloroethyl chloroacetate*, b. p. 94—95°/12 mm.,

from chloroacetyl chloride at 100°, *β-chloroethyl benzoate*, b. p. 120—122°/5 mm., from benzoyl chloride at 190—240°, *β-chloroethyl* p-*nitrobenzoate*, yellow crystals, m. p. 56°, from *p*-nitrobenzoyl chloride at 190—240°, and *β-bromoethyl acetate*, b. p. 163°, from a mixture of equimolecular proportions of ethylene oxide and acetyl bromide kept for several hours at the ordinary temperature. G. F. M.

Colloid-chemical Studies on Soaps. Non-aqueous Lyophilic Soap Colloids. Martin H. Fischer (*Chem. Eng.*, 1919, **27**, 184—193).—The solvation capacities of various sodium soaps of the acetic series were determined. One gram-mol. of sodium arachidate will take up 27·5 litres of ethyl alcohol and still form a non-syneretic gel. The capacity of the lower members of the series becomes less as the molecular weight of the soap decreases. When a given soap is employed with different alcohols, the solvation capacity increases as the molecular weight of the alcohol becomes greater. The author has elaborated his theory of lyophilic and lyophobic colloids. The theory of soap gels is also dealt with. According to this, soaps form (*A*) true solutions in a solvent at higher temperatures. On the other hand, (*D*), a gel, when the temperature is low, is a true solution of the solvent in the solvated soap. Between these two extremes there exist two stages, (*B*) solvated soap dispersed in the solvent, (*C*) dispersed solvent in the solvated soap. If the temperature of *A* is lowered, all these stages are obtained. This is also true when the temperature of *D* is raised. The ranges of temperature in which *B* or *C* exists are not necessarily the same when the temperature of *A* is being lowered as when the temperature of *D* is being raised, because of a hysteresis effect. There exists, therefore, a region of ambiguity which depends on the previous history of the system. Gelation capacity is for these reasons not synonymous with solvation capacity. The latter is the phenomenon generally known as swelling, which is a different process from liquefaction. Chemical Abstracts.

Colloid-chemical Studies on Soaps. Martin H. Fischer and Marion O. Hooker (*Chem. Eng.*, 1919, **27**, 223—232. Compare preceding abstract.)—Solutions of sodium or potassium hydroxide of various concentrations are added to a standard aqueous solution of potassium oleate having the consistency of a syrup. As the concentration of the base is increased, the viscosity becomes greater until a gel is formed. Further addition of the base causes the soap to separate and the viscosity to fall rapidly. The separation of the soap occurs at a lower concentration for sodium hydroxide than for potassium hydroxide. The addition of aqueous ammonia always lowers the viscosity, the authors' explanation being that ammonium soaps are more soluble in water and are better solvents for water. Similar results are obtained when a sodium or potassium salt is added in place of the hydroxide, except that potassium acetate has a much greater salting-out effect than the chloride, nitrate, etc. Ammonium salts, on the other hand, emulsify the

soap, but do not salt it out. Calcium or magnesium salts form insoluble or less hydrated soaps, and therefore the viscosity steadily decreases as more of the salt is added. Salts of the heavy metals such as copper or iron, cause the soap to separate in hard lumps. The effect is additive when potassium hydroxide or a potassium salt is also added. CHEMICAL ABSTRACTS.

Oleates and Stearates of certain Metals. MATHEUS D'ANDRADE ALBUQUERQUE (*Revista Chim. pura appl*, 1916, [ii] 1, reprint, 8 pp.).—The oleates and stearates of a number of metals were prepared by double decomposition of solutions of their salts with alkali soaps. The ethereal solutions of some of the metallic soaps oxidised on exposure to air; the action of hydrogen peroxide on the ethereal solutions was also ascertained.

Metal.	Colour of ethereal solution.	Oxidation by air to—	Oxidation by H_2O_2 to—	Stability of peroxidised solution.
Ag′	colourless	—	pale yellow	—
Cu′	amber-yellow	bluish-green	—	—
Cu″	bluish-green	—	yellowish-brown	unstable
Hg′	colourless	—	no colour change	—
Hg″	colourless	—	no change	—
Mn″	almost colourless	—	dark chestnut	stable
Co″	red	dark green	dark green	stable
Pb″	colourless	—	orange-yellow	very unstable
Cr″	pink	violet	violet	—
Cr‴	violet	—	no change	—
V″	*violet (?)*	*green (at once)*	*not given*	—

Titanium soaps could not be obtained. The cuprous compounds were made from cupric soaps by reduction with hydrazine sulphate as well as by the action of alkali stearate and oleate on moist cuprous chloride. The silver compounds were darkened by light. By means of the ethereal soap solutions, it was possible to observe the absorption spectra of the various metals in the non-ionised state. The chromic compounds showed a strong absorption in the yellow. W. R. S.

[Preparation of] Maleic Acid from Benzoquinone by Catalytic Oxidation. J. M. WEISS and C. R. DOWNS (U.S. Pat. 1318632).—Maleic acid is produced by dissolving benzoquinone in benzene and subjecting the mixture in the vapour phase to catalytic oxidation under conditions as described in U.S. Pat. 1318631 (this vol., i, 236). Inert diluent gases may be employed to control the reaction. In the condensate obtained from the reaction products there is usually present *benzoquinone*, *maleic acid*, *benzene*, *form aldehyde*, water, and various other by-products.

CHEMICAL ABSTRACTS.

[Preparation of] Maleic Acid by Catalytic Oxidation of Benzene. J. M. WEISS and C. R. DOWNS (U.S. Pat. 1318633).—The patent relates to a method of the same character as that described above (preceding abstract), preferably operating at 300—550°, with subsequent recovery of maleic acid as the main

product. When equal weights of benzene vapour and air are passed over vanadium oxide as a catalyst at such a velocity that the mixture stays in contact with the catalyst about 0·25 sec., a maximum yield of maleic acid is obtained by maintaining the *catalyst at 400—450°.* CHEMICAL ABSTRACTS.

The Mode of Pyrogenic Decomposition at High Temperature of Acetaldehyde, Metacetaldehyde, and Ethyl Alcohol. (MLLE.) EGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1920, [iv], **27**, 34—39).—When acetaldehyde is submitted to a high temperature for a very short time, the main decomposition is its conversion into carbon monoxide and methane, the molecule thus undergoing the least deformation possible. A second reaction proceeding at the same time, but to a less extent, yields carbon monoxide, ethylene, and oxygen. If the time of heating is prolonged, other secondary products, such as acetylene and benzene, appear.

Metacetaldehyde, under similar conditions, is first depolymerised to *give acetaldehyde, which then undergoes the changes given* above. In the case of ethyl alcohol, the principal reaction is its oxidation to acetaldehyde, which then undergoes pyrogenic decomposition, as described. A second reaction proceeding simultaneously, but to a lesser extent, results in the conversion of the alcohol into ethylene and water. W. G.

A Keto-glycol Derived from Mesityl Oxide. J. PASTUREAU and CH. LAUNAY (*Bull. Soc. chim.*, 1919, [iv], **25**, 593—597).—The crystalline compound, m. p. 123°, obtained by Wolffenstein (compare A., 1895, i, 644) by the action of hydrogen peroxide on mesityl oxide, is shown to be not a glycol, as described by him, but a peroxide of mesityl oxide, $CH_3\cdot CO\cdot CH<\begin{matrix}\text{———O} \\ CMe_2\cdot O\end{matrix}$, and on hydrolysis it loses oxygen and gives the glycol of mesityl oxide described by Harries and Pappos (compare A., 1901, i, 673). W. G.

Lactose. J. GILLIS (*Rec. trav. chim.*, 1920, **39**, 88—125).—A more detailed account of work already published (compare A., 1918, i, 101, 155). W. G.

Lignin. ERIK HÄGGLUND (*Arkiv. Kem. Min. Geol.*, 1918–1919, **7**, No. 8, 1—20).—Reviewing the results of previous workers, the author attaches most importance to those of Klason (A., 1908, i, 717, and *Svensk Papperstidning*, 1916, No. 17), derived from a study of the ligninsulphonic acids; but the regeneration of lignin from these derivatives by means of 70% sulphuric acid, a method also used by Koenig (*Chem. Zeit.*, 1912, **36**, 1101), requires one to two hours, and is accompanied by considerable decomposition of the lignin. The author now finds that 28% by weight of the wood of "hydrochloric acid-lignin" is obtained by shaking 1 part of finely powdered pine wood with 10 parts of 43% hydrochloric acid for fifteen minutes, rapidly filtering, and washing the residue free from hydrochloric acid. The product is a

pale brown powder with a strong odour of vanillin, and contains 1·63% of combined chlorine. It gives a deep purple colour with phloroglucinol in hydrochloric acid solution, a pale yellow colour with aniline sulphate, a dark red colour with *p*-phenylenedimethyldiamine sulphate, a dark blue colour with equal parts of potassium ferricyanide and ferric chloride, but no precipitate with Maule's reagent. A comparison of its methoxyl content with that of the original wood shows that about 20% of this is split off during the hydrochloric acid treatment. After introducing a corresponding correction, the author's analytical results agree with Klason's formula, $(C_{40}H_{40}O_{11})_n$, for lignin, but not with those of Cross and Bevan ("Cellulose," iii) or of Green (Schwalbe, "Chemie der Cellulose," 1911, 448). Protocatechuic acid was identified among the products of fusion of hydrochloric acid-lignin with potassium hydroxide and lead peroxide, but acetic acid, oxalic acid, and catechol could not be detected. The formation of these products from wood (Lange, A., 1890, 228) is therefore due to other constituents than lignin. The author also investigated his product in regard to its furfuraldehyde content, solubility in bisulphites and in alkalis, the action of chlorine and bromine, its oxidation with alkaline permanganate and with potassium chlorate and nitric acid, and the results of dry distillation. J. K.

Salts of β-Hydroxytrimethylenediglycine and of *N*-Hydroxymethylglycine. Hugo Krause (*Ber.*, 1919, **52**, [*B*], 1211—1222).—The peculiarity (A., 1918, i, 156) attending the formation of the barium salt $(+3H_2O)$ of β-hydroxytrimethylenediglycine (the barium salt containing $1·5H_2O$ [A., 1918, i, 337] is now stated to be non-existent) has been examined. It is due to supersaturation, which, however, is not always operative; in many experiments a noteworthy retardation of the crystallisation was never observed when technical formalin reacted with a freshly prepared solution of barium glycine or when a solution of the latter which had been kept in the cold for an hour or longer was treated with formaldehyde solution containing or not containing methyl alcohol. The initiation of crystallisation by the addition of a little methyl alcohol (*loc. cit.*) cannot be regarded, therefore, as a proof that the alcohol plays a part in the reaction.

A second *barium* salt of the same composition,

$$C_7H_{12}O_5N_2Ba,3H_2O,$$

which is amorphous and extremely soluble in water, is obtained by treating a 25% solution of β-hydroxytrimethylenediglycine in formalin, which has been kept for a few days, with the theoretical quantity of a 15% paste of barium hydroxide, and adding 8 vols. of 80% methyl alcohol to the resulting, almost clear solution.

Some experiments on the simultaneous formation of the barium salts of β-hydroxytrimethylenediglycine and *N*-hydroxymethylglycine indicate that the production of the latter is favoured by working at low temperatures with pure formaldehyde, any considerable excess of which is to be avoided.

In addition to the salts of *N*-hydroxymethylglycine already described (*loc. cit.*; A., 1919, i, 67), the following have been prepared by the action of pure 33% *formaldehyde solution on the* metallic glycine salt: *potassium*, $OH\cdot CH_2\cdot NH\cdot CH_2\cdot CO_2K$, amorphous, brittle mass, which is obtained in a purer form by treating the normal lead salt with potassium sulphide; *sodium* (at 80° *in a vacuum these two salts* [2 mols.] appear to lose water [1 mol.], with the formation of anhydro-salts); *barium* ($+2H_2O$), microscopic rods; *calcium* ($+1H_2O$), hygroscopic, amorphous powder. The copper and lead salts must be dried over calcium chloride, not over sulphuric acid (*loc. cit.*), which causes loss, not only of water, but also of a little formaldehyde. C. S.

Behaviour of Carbamide towards Hydrogen Peroxide and a Simple Process for its Purification and Decoloration. HERMANN KUNZ-KRAUSE (*Kolloid Zeitsch.*, 1919, **25**, 240—241).—Carbamide is not affected in the slightest degree by boiling it in aqueous solution with hydrogen peroxide, but colloidal colouring matter, which is generally present in carbamide, is destroyed. Carbamide made from potassium cyanide which has been obtained from potassium ferrocyanide often exhibits a blue to green tint, which cannot be removed by recrystallisation. The colour is due to Prussian-blue, and is destroyed by boiling the carbamide with hydrogen peroxide. J. F. S.

Carboalkyloxythiocarbamides. AUGUSTUS EDWARD DIXON and RAYMOND THOMAS JOACHIM KENNEDY (T., 1920, **117**, 80—85).

Preparation and Separation of Cyanates Soluble in Water. J. D. RIEDEL (D.R.-P. 314629; from *Chem. Zentr.*, 1919, iv, 913).—Chlorine or bromine is directly added to highly concentrated alkaline solutions of cyanides; formation of cyanogen haloid only occurs to a subsidiary extent. Sodium cyanate is smoothly formed by this reaction, and is deposited in the solid state from its solution as the process goes forward. The product is applicable to technical and pharmaceutical purposes. H. W.

Free Thiocyanogen. ERIK SÖDERBÄCK (*Annalen*, 1919, **419**, 217—322).—The author discusses the unsuccessful attempts of Liebig (1829 and 1844), Linnemann (1861), and Schneider (1866) *to prepare thiocyanogen*. Klason's compound, $(CN)_3S_3\cdot S_3(CN)_3$, obtained in 1886, is a cyanuric derivative. Quite recently, Bjerrum and Kirschner have detected small quantities of thiocyanogen in aqueous solutions of complex gold thiocyanates, $MAu(SCN)_4$.

When an ethereal *N*- or *N*/10-solution of iodine is shaken with silver thiocyanate in excess, the colour of the iodine rapidly fades and yellow silver iodide is formed. The reaction, however, appears to reach a state of equilibrium. As it is impossible to separate completely the excess of iodine from the soluble product of the

reaction, the halogen is removed as far as possible by mercury and the pale yellowish-brown solution examined. As the author expected it to be a dilute solution of thiocyanogen and to behave analogously to the halogens, it was treated with (1) chlorides and bromides, whereby no appreciable effect was produced; (2) aqueous or alcoholic solutions of iodides (of cadmium, lead, silver, and mercury), whereby iodine was liberated; (3) iron powder, whereby ferric thiocyanate was produced in such quantity that the solution became opaque; (4) mercury, whereby mercurous thiocyanate was *formed; (5) cuprous thiocyanate, whereby black cupric thiocyanate* was formed; and (6) water, which slowly decomposed the thiocyanogen producing thiocyanic acid, hydrogen cyanide, and sulphuric acid.

The solvent ether can be replaced by acetone, absolute ethyl alcohol, chloroform, carbon tetrachloride, benzene, ethylene dibromide, or carbon disulphide. The reaction proceeds very slowly in the last solvent, but almost reaches completion in chloroform; in every case, however, a state of equilibrium appears to be attained.

The thiocyanates of potassium, zinc, cadmium, copper, and lead do not react appreciably with a solution of iodine, but mercuric thiocyanate reacts in the same way as silver thiocyanate.

Much better results are obtained with bromine. A solution of bromine in dry ethyl ether, ethyl chloride, ethyl bromide, carbon disulphide, carbon tetrachloride, chloroform, benzene, or ethylene dibromide reacts completely with the thiocyanates of silver, lead, cadmium, mercury, zinc, thallium, and copper in accordance with the *equation* $2MSCN + Br_2 = 2MBr + 2CNS$, *since the resulting solution* (in carbon disulphide or tetrachloride) is completely free from bromine, and in experiments with silver, lead, and mercury thiocyanates in which an excess of bromine was used, the solid product of the reaction is the pure metallic bromide. The velocity of the reaction is influenced by the solvent. A *N*-solution of bromine in carbon disulphide is decolorised by lead thiocyanate in slight excess within a few minutes, whilst about half an hour is necessary when the solvent is dry ether. A solution of bromine in carbon *disulphide dried with phosphoric oxide is not decolorised* by lead thiocyanate after one hour, but is almost instantly decolorised by silver or mercury thiocyanate.

The solutions of thiocyanogen obtained above are usually faintly yellow, but are occasionally quite colourless. The more concentrated solutions have a stinking odour resembling that of thiocyanic acid, and stain the skin pale red, changing to yellow. The solutions become turbid on keeping and deposit yellow or yellowish-red amorphous products. The decomposition proceeds slowly in ethyl *chloride or bromide or* ether, and very rapidly in carbon disulphide. S[illegible] amorphous products, which are different from different solvents, [illegible]r to be mixtures consisting chiefly of polythiocyanogen, [illegible]: about 1% of hydrogen is also present.

[illegible]e in carbon tetrachloride solution does not react with lead [illegible] but yields a solution of thiocyanogen and the corre-

sponding metallic chloride by shaking with an excess of silver or mercury thiocyanate; sulphur chloride and cyanogen chloride are not present in appreciable quantities in the resulting solution.

The author's usual practice for the preparation of a solution of thiocyanogen is to treat lead thiocyanate with a dry ethereal solution of bromine cooled by ice-water.

The evaporation in a vacuum over sulphuric acid of an approximately $N/2$-solution of thiocyanogen in ethyl chloride, bromide, or ether left a clear, viscous, unstable, yellow oil. By cooling an approximately $N/2$-solution in carbon disulphide to $-70°$, *thiocyanogen*, CNS, is obtained in cruciform aggregates of almost colourless crystals, m. p. $-3°$ to $-2°$. The molten substance can be supercooled to $-20°$, but always resolidifies at $-30°$, giving well-defined rhombic plates. By allowing it to warm to the ordinary temperature, thiocyanogen becomes reddish-brown and more viscous; finally, a yellow smoke is evolved and a dark brick red, amorphous solid is formed. Thiocyanogen dissolves extremely rapidly in ethyl alcohol or ether, but only slowly in carbon disulphide or tetrachloride. Thiocyanogen is at least as strongly electronegative as iodine.

A solution of thiocyanogen reacts with zinc and cadmium (solvent, carbon disulphide mixed with about one-fifth the volume of absolute ethyl alcohol) to form the respective thiocyanates; with mercury (solvent, carbon tetrachloride) to form mercurous thiocyanate; with aluminium (solvent, dry ether) to form an *etherate* of aluminium thiocyanate, $Al(SCN)_3,2Et_2O$, extremely hygroscopic, colourless plates, which become friable, and ultimately a syrup in air; with tin (solvent, carbon disulphide mixed with a small quantity of dry ether) to form an *etherate* of stannic thiocyanate, $Sn(SCN)_4,2Et_2O$, yellow, apparently prismatic, hygroscopic crystals, which change into a syrup in air; with arsenic (solvent, carbon disulphide) to form *arsenious thiocyanate*, $As(SCN)_3$, almost colourless crystals; with antimony (solvent, dry ether) to form an extremely hygroscopic antimony thiocyanate (not isolated); with an excess of iron (ferrum reductum) (solvent, dry ether) to form ferrous thiocyanate, and with a deficit of iron to form anhydrous ferric thiocyanate, dark violet, crystalline powder; with manganese (solvent, ether and alcohol) to form manganous thiocyanate; with nickel (solvent, carbon tetrachloride), cobalt (solvent, carbon disulphide and alcohol), and silver (solvent, ether) to form the respective metallic thiocyanates, and with gold (solvent, none) to form, apparently, a mixture of aurous and auric thiocyanates (not isolated). Many of the experiments with metals are of a qualitative nature only.

The molecular weight of thiocyanogen cannot yet be determined. It does not yield well-defined products by treatment with organo-magnesium compounds. In order to ascertain which of its three atoms is the reactive one, a solution in dry ether was treated with mercury diphenyl, whereby phenyl thiocyanate and phenyl mercurithiocyanate, Ph·Hg(SCN), m. p. 231—232·5° (Otto in 1870 gave m. p. 226—227°), were obtained: the latter was also obtained from

phenyl mercuri-iodide and thiocyanogen in carbon disulphide solution. Ethereal solutions of thiocyanogen and zinc ethyl react to form zinc thiocyanate and ethyl thiocyanate.

Thiocyanogen in solution does not yield well-defined products with ammonia or aliphatic amines, but in cold ethereal solution it reacts with aniline in accordance with the equation $2PhNH_2 + 2CNS = NCS{\cdot}C_6H_4{\cdot}NH_2 + PhNH_2,HSCN$ to form aniline thiocyanate and p-*thiocyanoaniline*, colourless, odourless needles (from water), m. p. 57—57·5°. When twice the quantity of thiocyanogen is used, the product is p-*thiocyanoaniline thiocyanate*, faintly red crystals. By reduction with hydrochloric acid and zinc dust, *p*-thiocyanoaniline yields *p*-aminophenyl mercaptan, which was identified by oxidation to the corresponding disulphide. In a similar manner, thiocyanogen and dimethylaniline react in ethereal solution to form dimethylaniline thiocyanate and p-*thiocyanodimethylaniline*, $NMe_2{\cdot}C_6H_4{\cdot}SCN$, colourless, odourless crystals, m. p. 73—74°, which yields *p*-dimethylaminophenyl mercaptan by reduction. Diphenylamine and thiocyanogen in ethereal solution yield thiocyanic acid and ? : ?-*dithiocyanodiphenylamine*, $NH(C_6H_4{\cdot}SCN)_2$, faintly greenish-yellow needles, m. p. 120°, whilst triphenylamine under similar conditions yields thiocyanic acid and ? : ?-*dithiocyanotriphenylamine*, needles, m. p. 115—116°.

Phenol and thiocyanogen in carbon disulphide solution react to form thiocyanic acid (which was not detected, however, being apparently converted by a secondary reaction into an insoluble, yellowish-brown substance) and p-*thiocyanophenol*, colourless, odourless plates of rhombic habit, m. p. 53—54°, the constitution of which was proved by its conversion through *p*-hydroxyphenyl mercaptan into *pp'*-dihydroxydiphenyl disulphide, and also by its formation from *p*-thiocyanoaniline by the diazo-reaction.

Some experiments on the competition of iodine and thiocyanogen in solution for a metal show that the equilibrium $MSCN + I \rightleftharpoons MI + CNS$ is largely dependent on the nature of the metal; in the case of cadmium, the reaction from right to left is practically irreversible.

Stannous thiocyanate, produced by the interaction of lead thiocyanate and stannous sulphate in aqueous solution, and obtained in colourless crystals from the hot filtrate after removing lead sulphate, is converted into the etherate of stannic thiocyanate by a solution of thiocyanogen in a mixture of carbon disulphide and ether.

An ethereal solution of thiocyanogen reacts with mercuric cyanide (and also with silver or zinc cyanide) to form mercuric thiocyanate and a substance which is identical with the cyanogen sulphide, $(CN)_2S$, described by Linnemann and by Schneider; from this method of preparation, the substance might be cyanogen thiocyanate, $CN{\cdot}SCN$.

Several investigators have recorded the production of a very unstable, blood-red substance when a concentrated aqueous solution of potassium thiocyanate is acidified with sulphuric acid and treated

with a solution of sodium nitrite. This substance, which almost immediately decomposes, with the evolution of nitric oxide, can also be obtained by treating a solution of nitrosyl chloride in carbon tetrachloride with silver thiocyanate at the ordinary temperature. It appears to be *nitrosyl thiocyanate*, NO·SCN, since its solution, which is relatively stable at $-17°$, converts cuprous thiocyanate into cupric thiocyanate and metallic mercury into mercurous thiocyanate, and reacts with aqueous sodium hydroxide to form sodium thiocyanate and sodium nitrite. The author has performed some preliminary experiments in which the substance is produced from nitric oxide and thiocyanogen in well-cooled carbon disulphide. The substance allies itself with the nitrosyl haloids in its properties, its position falling between those of the bromide and iodide.

Although its molecular weight cannot yet be ascertained, the author is of opinion that the molecular magnitude and the constitution of thiocyanogen in solution are represented by the formula CN·S·S·CN. In accordance with this nitrile structure, a dry ethereal solution of thiocyanogen reacts with dry ethereal hydrogen chloride cooled with ice-water to form a precipitate of a colourless, crystalline *substance*, 2CNS,2HCl (which becomes yellow above 100° and changes gradually to a brown substance without melting), and a solution of a *substance*, 2CNS.HCl, pale yellow prisms or plates of rhombic habit, m. p. 69—70°. In contrast to the former, the latter substance, which is not formed when carbon disulphide, carbon tetrachloride, chloroform, or benzene is employed as solvent, is easily soluble in organic solvents and is unaffected by hot water. The substance, 2CNS,2HCl, is converted by water into a *substance*, pale yellow, rhombic leaflets or needles, which decomposes without melting when heated, and has the composition of thiocyanogen hydrate, $(CNS)_2.H_2O$. The latter substance is regarded as 2-*imino-5-keto-1:3:4-dithioazolidine*, $NH<\begin{matrix}CO——S\\C(:NH)·S\end{matrix}$, since it presents several points of analogy to perthiocyanic acid (2-imino-5-thio-1:3:4-dithioazolidine; Hantzsch and Wolvekamp, A., 1904, i, 718), particularly in its behaviour with cold aqueous potassium hydroxide, whereby sulphur is liberated and a colourless, crystalline *substance*, $C_2ON_2SK_2$ (*potassium cyanoiminothiocarbonate*, CN·N:C[SK]·OK), analogous to potassium dithiocyanate (cyanoiminodithiocarbonate), produced. The substance 2CNS,2HCl is probably 5:5-dichloro-2-imino-1 : 3 : 4-dithioazolidine, $NH<\begin{matrix}CCl_2——S\\C(:NH)·S\end{matrix}$. When suspended in benzene, it reacts with aniline to form the hydrated hydrochloride of Fromm's thiuret (A., 1893, i, 575), $C_8H_7N_3S_2$,HCl,$3H_2O$.

C. S

Photochemical Oxidation of Potassium Thiocyanate. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1919, **58**, 457—463).—Under the influence of sunlight, aqueous potassium thiocyanate solutions undergo change, in which the atmospheric oxygen takes

part. With solutions of medium concentration, this change takes place with great rapidity, an *amorphous, yellow precipitate of* pseudocyanogen sulphide separating in most cases; if the concentration is either above or below a certain limiting value, the change is either entirely prevented or proceeds only very slowly. The concentration of the thiocyanate most favourable to the separation of pseudocyanogen sulphide is about 50% in the summer and about 10% in the winter. The purer potassium thiocyanates, especially those quite free from traces of ferrous salts, are more sensitive to this reaction than less pure preparations.

In addition to pseudocyanogen sulphide, the photochemical decomposition of potassium thiocyanate yields as constant products hydrocyanic and sulphuric acids, carbon dioxide, and ammonium salts, $12KCNS + 12O_2 + 6H_2O = 6K_2SO_4 + 3HCN + 3CO_2 + 3NH_3 + 2(CNS)_3$. Further, there is always formed an unstable, intermediate peroxygenated compound, which imparts a blue colour to fresh guaiacum tincture, and is possibly analogous to Caro's acid.

Normal, decinormal, and centinormal solutions of potassium thiocyanate undergo these alterations, but only with the first of these does separation of pseudocyanogen sulphide take place. Although decomposed in this way, the deci- and centi-normal solutions show, within certain limits of time, no sensible diminution in titre, probably owing to the replacement, at least in the early stages of the change, of the thiocyanate by an equivalent proportion of the cyanide.

T. H. P.

Direct Passage from the Nitrous Esters and Nitro-compounds to Nitriles by Catalysis. ALPH. MAILHE and (MME) M. L. BELLEGARDE (*Bull. Soc. chim.*, 1919, [iv], **25**, 588—593).—By the catalytic hydrogenation of *iso*amyl nitrite by means of reduced nickel at 280°, primary, secondary, and tertiary amines result, with a small amount of *iso*valeronitrile. If the temperature of hydrogenation is increased to 300—320°, the yield of nitrile is considerably increased at the expense of the amines. At the same time, a certain amount of *iso*amyl alcohol is obtained, owing to hydrolysis of some of the nitrite, and a portion of the alcohol then nndergoes dehydrogenation, giving the corresponding aldehyde. Similar results were obtained with propyl, *iso*butyl, and heptyl nitrites.

In the same way, at temperatures above 300°, nitromethane gave some hydrogen cyanide and nitropentane some *iso*valeronitrile.

W. G.

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sul **Fixation of Nitrogen in the Form of Hydrogen Cyanide**
this **means of an Electric Arc.** E. BRINER and A. BAERFUSS
thiocy. *Chim. Acta*, 1919, **2**, 663—666).—Mixtures of hydrocarbons
Seveitrogen when submitted to the action of an electric arc pro-
unstable drogen cyanide in yields much superior to the yield of
of potassi obtained from nitrogen and hydrogen. The method
is similar to that previously described (A., 1919, ii, 338).

The mixture of gases circulates at the rate of 8—10 litres per hour in a chamber where an arc of 0·020 amp. is burning between platinum electrodes 7 mm. apart. Using 12 parts of methane, 23 of nitrogen, and 65 of hydrogen under 635 mm. pressure, 0·08% by volume of hydrogen cyanide is obtained. This gives a yield of 0·46 gram of hydrogen cyanide per kilowatt hour, in addition to a yield of 0·14 gram of ammonia per kilowatt hour. In this case, the *E.M.F.* applied was 1020 volts. With the same mixture, but with an *E.M.F.* of 420 volts, 0·12% by volume of hydrogen cyanide was obtained, which is 1·75 gram per *K.W.H.* and 0·44 gram of ammonia per *K.W.H.* The best case examined is with a mixture of 1 part of methane and 5 of nitrogen at 505 volts, where a yield of 0·75% by volume of hydrogen cyanide was obtained, which is 7·39 grams of hydrogen cyanide per *K.W.H.* and 0·48 gram of ammonia per *K.W.H.* J. F. S.

Action of Carbon Monoxide on Sodium Alkyls. WALTER SCHOELLER, WALTER SCHRAUTH, and WALTER ESSERS (*Ber.*, 1920, **53**, [*B*], 62—63).—In reference to Schlubach's communication on this subject (this vol., i, 19), reference is given to earlier work by the authors on the action of carbon monoxide on mercury acetate (A., 1913, i, 1162). J. C. W.

Preparation of *o*-Divinylbenzene. JULIUS VON BRAUN and LUDWIG NEUMANN (*Ber.*, 1920, **53**, [*B*], 109—113).—The pure methiodide of *o*-di(-*β*-dimethylaminoethyl)benzene,

$$NMe_2\cdot C_2H_4\cdot C_6H_4\cdot C_2H_4\cdot NMe_3I,$$

has m. p. 196°, and not 175—185° as previously stated (A., 1917, i, 130). When boiled with sodium hydroxide in a current of steam, the salt is decomposed into an amorphous, pale yellow *polymeride* of *o-divinylbenzene*, $C_6H_4(CH{:}CH_2)_2$, m. p. 206—207°, and also *β-o-vinylphenylethyldimethylamine*,

$$CH_2{:}CH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2,$$

which passes over in the steam. The base has b. p. 123—124°/13 mm., and forms a *picrate*, yellow leaflets, m. p. 137°, a *platinichloride*, m. p. 167°, and a silvery *methiodide*, m. p. 209°. The corresponding quaternary ammonium hydroxide is stable in solution, but yields the above polymeride on evaporation. Seeing that the isolated unsaturated base is so stable, it appears that the extensive decomposition which it suffers in the above reaction is "induced" by the decomposition of the other group. J. C. W.

The Two Isomeric Diphenylindenes. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], **25**, 598—600).—The author shows that the diphenylindene obtained by him by the action of heat on *αβγ*-triphenylpropene dibromide (compare A., 1914, i, 265) is really the *αβ*-diphenylpropene, and that during the formation of its benzylidene derivative or its oximino-derivative it undergoes isomerisation to the *βγ*-diphenylindene described by Thiele and Ruggli (compare A., 1912, i, 866). W. G.

Action of Light on I-10-Bromophenanthrene-3(or 6)-sulphonic Acid. HÅKAN SANDQVIST (*Arkiv Kem. Min. Geol.*, 1917–18, **7**, No. 4, 1—14).—In a previous paper (A., 1915, i, 795), the author has shown that the action of light on aqueous solutions of 10-bromophenanthrene-3(or 6)-sulphonic acid in hydrochloric acid decreases the viscosity of the solution, and has explained this as being due to the light changing an *a*-form of the acid into the *b*-form. Each form was supposed to give salts with different solubilities, water of crystallisation, etc., but the further experiments of the author with the barium salt have not led to the isolation of two such isomerides. However, from the more soluble fractions of the barium salt, which had been exposed to an intense light, a reddish-brown to black, varnish-like acid was obtained, which immediately lowered the viscosity of a sulphonic acid–hydrochloric acid mixture when added to it. From this dark acid, the dimethyl ester was prepared, and analysis showed it to be *dimethyl monobromodiphenanthryldisulphonate* (annexed formula); the *barium* salt was $C_{28}H_{15}Br(SO_3)_2Ba$. It is the production of this acid by the action of light (oxidation) on the original sulphonic acid which causes the decrease in viscosity; the addition of 0·02% to the sulphonic acid–hydrochloric acid solution lowers the viscosity to one-third of its former value.

$$\begin{array}{l}(?)\,C_{14}H_7{<}^{Br}_{SO_3Me\ (3\ \text{or}\ 6)}\\ \quad\ \ |\\ (10')\,C_{14}H_8{-}SO_3Me\ (3'\ \text{or}\ 6')\end{array}$$

From the mother liquors of the above-mentioned barium salt another substance was isolated, but not identified, which lowered the viscosity, but not to such a great extent. Phenanthraquinone-3-sulphonic acid exerts a still less effect. The product formed, together with II-10-bromophenanthrene-3(or 6)-sulphonic acid in the bromination of phenanthrene-3-sulphonic acid (*ibid.*, 1917, **6**, No. 13, 13) has exactly the same effect as the above-mentioned product of the action of light, and is therefore probably the same substance.

It is shown experimentally that the presence of monobromodiphenanthyldisulphonic acid or its barium salt accounts for the differences in solubility, etc., described in the previous paper (*loc. cit.*). T. S. P.

Amine Oxidation. I. Oxidation of Aniline. STEFAN GOLDSCHMIDT (*Ber.*, 1920, **53**, [*B*], 28—44).—In Bamberger's interpretation of the oxidation of aniline, phenylhydroxylamine is regarded as the initial product. Whilst this compound may very well lead ultimately to nitrobenzene, it does not offer a satisfactory explanation of the formation of the polynuclear oxidation products, since it is not sufficiently reactive. It has been shown, however that benzoquinonephenyldi-imine, which is regarded as the pre cursor of aniline-black, and azobenzene, are the first demonstrabl products of the oxidation by alkaline permanganate or bleachin powder, whereas these are not formed under conditions appropria

benzene. It appears, therefore, that there are two different initial products, varying according to the conditions. Agents which readily yield atomic oxygen, such as Caro's acid or hydrogen peroxide, produce aniline oxide, and further developments follow as in the scheme: $PhNH_2 \longrightarrow PhNH_2{:}O \longrightarrow PhNH{\cdot}OH \longrightarrow PhNO \longrightarrow PhNO_2$, and $PhNO + PhNH{\cdot}OH \longrightarrow PhN{-}{-}NPh$ (bridged by O), and $PhNO + PhNH_2 = PhN{:}NPh$. Under other conditions, however, the initial stage is represented by the removal of two atoms of hydrogen, subsequent changes being due to the activity of the PhN: residue (compare A., 1913, i, 1173). This radicle may, for example, polymerise to azobenzene, benzoquinonephenyldi-imine, $NPh{:}C_6H_4{:}NH$, or emeraldine. This assumption is based on the fact that azo-compounds and quinonearyldi-imines can be isolated when aniline, and especially its nuclear-substituted methyl homologues having free para-positions, are oxidised by lead peroxide. The theory is considerably strengthened by the further fact that mixed azo-compounds and mixed quinonearyldi-imines are produced when two amines are oxidised together.

The methylated quinonearyldi-imines are easily hydrolysed by acids to the original amine and the quinone, and may thus be identified. They differ, therefore, from unsubstituted benzoquinonephenyldi-imine, which mainly polymerises to emeraldine. This explains, therefore, why Willstätter obtained only duroquinone in an attempt to oxidise aminodurene in acid solution to a methylated emeraldine (A., 1909, i, 899).

In the oxidation of aniline itself, the base is dissolved in ether and shaken with lead peroxide and anhydrous sodium sulphate. The filtered oxidation products are then shaken with alcohol, ammonium chloride, and zinc dust to reduce the benzoquinonephenyldi-imine to *p*-aminodiphenylamine. A current of steam removes unchanged aniline and azobenzene, whilst the diamine is isolated as the sulphate. In the other cases, the ethereal solution is oxidised by lead peroxide and glacial acetic acid, the di-imine is then reduced by zinc dust, and the colourless solution is shaken with sodium carbonate to remove acetic acid. The dry ethereal solution is finally mixed with alcoholic oxalic acid to precipitate the oxalate of the aminodiarylamine.

Aminodidurylamine, $C_{20}H_{28}N_2$, crystallises in concentric groups of needles, m. p. 157°, and may be oxidised by lead peroxide to *duroquinonedurylidi-imine*, $C_6HMe_4{\cdot}N{:}C_6Me_4{:}NH$, druses of reddish-brown needles, m. p. 155—156°, which yields aminodurene and *p*-duroquinone, m. p. 110°, when mixed with an excess of hydrochloric acid.

1-Amino-2:3:5-cumene gives rise to *azocumene* [2:3:5:2′:3′:5′-*hexamethylazobenzene*], m. p. 152—153°, *aminodicumylamine*, $C_{18}H_{24}N_2$, m. p. 138—139°, and *cumoquinonecumyldi-imine*, $C_6H_2Me_3{\cdot}N{:}C_6HMe_3{:}NH$, stout prisms, m. p. 103°.

From *m*-4-xylidine are prepared azoxylene (2:3:2′:3′-tetramethylazobenzene), m. p. 111°, *aminodixylylamine* [4-*amino*-

2 : 3 : 2′ : 3′-*tetramethyldiphenylamine*], m. p. 74—75°, and *xyl*[...] *quinonexylyldi-imine*, brown rosettes, m. p. 67·5—68·5°.

The oxidation of a mixture of aminodurene and *m*-4-xylidine i[s] described. The isolation of the products presents some difficultie[s] but *xylylaminodurylamine* [4-*amino*-2 : 3 : 5 : 6 : 2′ : 3′-*hexamethyldi*-*phenylamine*], m. p. 153—154°, is certainly identified by its oxida-tion to *duroquinonexylyldi-imine*, m. p. 83—84°, and hydrolysis o[f] this to duroquinone and the xylidine. *Azodurene* is also present it forms reddish-yellow tablets, m. p. 80—81°. J. C. W.

Intramolecular Rearrangement of the Alkylarylamines Formation of 4-Amino-*n*-butylbenzene. JOSEPH REILLY an[d] WILFRED JOHN HICKINBOTTOM (T., 1920, **117**, 103—137).

New Method for the Preparation of Alkylamines. JIR[O] TAKEDA and SAJURO KURODA (*J. Pharm. Japan*, 1919, **449** 561—608).—Styrene dibromide and carbamide react at 120—130° to form 2-*amino*-4-*phenyl*-4 : 5-*dihydro-oxazole*, $O<\begin{matrix}CH_2—CHPh\\C(NH_2){:}N\end{matrix}$ the hydrolysis of which by alcoholic potassium hydroxide at 150° yields ammonia and *β-hydroxy-α-phenylethylamine*,

$$NH_2{\cdot}CHPh{\cdot}CH_2{\cdot}OH,$$

the *dibenzoyl* derivative, m. p. 155°, of which has also been pre-pared by the following series of reactions, which prove its constitu-tion: $COPh{\cdot}CH_2Br \longrightarrow COPh{\cdot}CH_2{\cdot}OAc \longrightarrow COPh{\cdot}CH_2{\cdot}OH \longrightarrow NOH{:}CPh{\cdot}CH_2{\cdot}OH \longrightarrow NH_2{\cdot}CHPh{\cdot}CH_2{\cdot}OH \longrightarrow NHBz{\cdot}CHPh{\cdot}CH_2{\cdot}OBz$

On the assumption that the reactions proceed analogously to th[e] preceding, anethole dibromide heated with half its weight of carb-amide at 120—130° yields 2-*amino*-4-p-*anisyl*-5-*methyl*-4 : 5-*dihydro-oxazole*, $OMe{\cdot}C_6H_4{\cdot}CH<\begin{matrix}N{=\!=}C{\cdot}NH_2\\CHMe{\cdot}O\end{matrix}$, rectangular columns, m. p. 165°, the hydrolysis of which by alcoholic potassium hydroxide produces ammonia and *β-hydroxy-α-p-anisylpropylamine*,

$$OH{\cdot}CHMe{\cdot}CH(NH_2){\cdot}C_6H_4{\cdot}OMe$$

(*hydrochloride*, m. p. 193°; *copper* derivative, m. p. 113°). Bromo-anethole dibromide and *iso*safrole dibromide also react with carb-amide, yielding corresponding oxazolines, m. p. 20° and 175° respectively. CHEMICAL ABSTRACTS.

Ketens. XXX. Preparation of a Keten-imine Derivative from Diphenylketen. H. STAUDINGER and JULES MEYER (*Ber.*, 1920, **53**, [*B*], 72—76).—Triphenylphosphinephenylimine (this vol., i, 107) reacts with diphenylketen in benzene solution in an atmo-sphere of nitrogen to form triphenylphosphine oxide (I) and diphenylketenphenylimine (II), thus:

$$PPh_3{:}NPh + CPh_2{:}CO = \begin{matrix}PPh_3{\cdot}NPh\\ | \quad\quad |\\ O—C{:}CPh_2\end{matrix} \longrightarrow \underset{(I.)}{O{:}PPh_3} \text{ and } \underset{(II.)}{NPh{:}C{:}CPh_2}$$

The same products are formed when triphenylphosphinediphenylmethylene (*ibid.*, 106) is treated with phenylcarbimide, thus:

$$PPh_3{:}CPh_2 + NPh{:}CO = \begin{array}{l} PPh_3\cdot CPh_2 \\ \,|\qquad\quad | \\ O \text{———} C{:}NPh \\ \qquad\downarrow \\ \text{(I.) and (II.)} \end{array},$$

In either case, the oxide is precipitated by the addition of light petroleum.

Diphenylketenphenylimine crystallises in transparent, pale yellow tablets, m. p. 55—56°, b. p. 190—195°/abs. vac. It has been sought for some time, in order to compare its properties with those of compounds with other systems of twin double linkings, such as ketens, –C:C:O, and carbimides, –N:C:O. Quite unexpectedly, the new compound, with the system –N:C:C=, is very stable and resistant to air, water, alcohol, and bases. When warmed with concentrated hydrochloric acid, however, it yields diphenylacetanilide. J. C. W.

Certain Completely Substituted Aromatic Iminosulphides. H. Rivier and Ch. Schneider (*Helv. Chim. Acta*, 1920, **3**, 115—134).—The authors give an extended review of the literature relating to the formation of substances containing the group C–S–C=N, and their isomerides with the group C–N–C=S. The possibility of assigning definite formulæ to the substances is based on the fact that the chromophore, C=S, is much more active than the group, C–S–C. From this point of view, the authors have revised and extended the work of Jamieson (A., 1904, i, 396), and have prepared a series of compounds which are either yellow or red, and which are therefore held to contain the groups –C–S–C– and C=S respectively. In only one case has the direct conversion of one form into the other proved possible, but a general consideration of the constitution of the products which have been isolated appears to justify the conclusion that stability is conditioned by symmetry of the molecule. It is, however, remarkable that in the sole instance of actual transformability, conversion is from the symmetrical to the less symmetrical form.

Benzanilide sulphide, NPh:CPh·S·CPh:NPh, intensely yellow prisms, m. p. 211—212° (Jamieson, *loc. cit.*; Raffo and Rossi, A., 1915, i, 86, give 202—204°), is most conveniently prepared by the action of benzanilideiminochloride on the potassium salt of thiobenzanilide. It is converted by hydrogen chloride in ethereal solution into the corresponding *chloride*, an amorphous, red mass, which is decomposed on exposure to moist air.

α-Thiobenznaphthalide, yellow crystals, m. p. 149—150°, and *β-thiobenznaphthalide*, yellow leaflets, m. p. 160—162°, are prepared by the action of phosphorus pentasulphide on a solution of the corresponding benznaphthalides in solvent naphtha. *α-Benznaphthalide sulphide*, $S(CPh{:}N\cdot C_{10}H_7)_2$, yellow, crystalline powder, m. p. 130—131°, is formed in the same manner as benzanilide

sulphide; when its solutions are boiled for some time or are evaporated, it becomes transformed into *thiobenzoyldi-α-naphthylbenzenylamidine*, $C_{10}H_7·N:CPh·N(C_{10}H_7)·CPh:S$, red crystals, m. p. 156—157°, but the reverse change could not be effected. Hydrogen chloride and concentrated sulphuric acid convert the yellow substance into red salts, which are decomposed by excess of acid, whilst the red material is decomposed by acid, with formation of benznaphthalide and thiobenznaphthalide. The action of benzanilide iminochloride on potassium α-thiobenznaphthalide or of α-benznaphthalide iminochloride on potassium thiobenzanilide yields the *substance*, $NPh:CPh·S·CPh:N·C_{10}H_7$, yellow crystals, m. p. 176—177°, which yields an unstable, red *hydrochloride*, which is decomposed by excess of acid into thiobenzanilide and α-benznaphthalide, showing that in the transformation which precedes the decomposition, it is the group NPh, and not $N·C_{10}H_7$, which has exchanged places with the sulphur atom. Attempts to prepare β-benznaphthalide sulphide or the sulphide of benzanilide and β-benznaphthalide were unsuccessful. p-*Dimethylaminobenzanilide sulphide*, $S[C(C_6H_4·NMe_2):NPh]_2$, yellow needles or prisms, m. p. 155—156°, is best prepared by the action of potassium sulphide on *p*-dimethylaminobenzanilideiminochloride hydrochloride; it yields a yellow, crystalline *hydrochloride*,

$$C_{30}H_{30}N_4S,2HCl.$$

Excess of hydrochloric or sulphuric acid does not decompose the salts, which thus appear to have the same constitution as the free base.

The action of thiobenzoyl chloride, Ph·CSCl, on diphenylbenzenylamidine, on *di-α-naphthylbenzenylamidine*, pale yellow leaflets, m. p. 160—161°, and on di-β-naphthylbenzenylamidine, colourless crystals, m. p. 154—155°, has been investigated; in the first case, benzanilide sulphide was obtained, whilst positive results were not given by the naphthalene derivatives.

Benzoylthiobenzanilide, COPh·NPh·CSPh, red prisms, m. p. 108—109° (compare Jamieson, *loc. cit.*), *benzoyl-α-thiobenznaphthalide*, red crystals, m. p. 145—146°, and *benzoyl-β-thiobenznaphthalide*, red crystals, m. p. 129—130°, were prepared by the gradual addition of a solution of benzoyl chloride in chloroform to the requisite thioanilide or thiobenznaphthalide dissolved in the calculated quantity of alcoholic potassium hydroxide. They are decomposed by hydrogen chloride in ethereal solution, even if only one molecular proportion of the acid is used, yielding benzoyl chloride and the corresponding thioanilide. They are soluble in concentrated sulphuric acid without decomposition, but addition of water precipitates the thioanilide. H. W.

[Preparation of] Phenolic Compounds. E. H. ZOLLINGER and H. ROEHLING (U.S. Pat. 1321271).—Lead compounds which form insoluble or sparingly soluble compounds with phenols are made to react with aromatic halogen compounds and a hydroxide of an alkali or alkaline earth metal. The reaction is facilitated by

catalysts, such as copper or copper compounds, iodides of alkali or alkaline earth metals, iodates, vanadium, titanium, molybdenum, and rare earths and their salts. Thus *o*-chlorophenol is heated for about forty-five minutes at 250° with an aqueous solution of lead acetate and sodium hydroxide (alternatively, lead sulphate or hydroxide at 260° with copper iodide as catalyst), whereby the lead salt of catechol is formed, which crystallises on cooling.

Among the examples recorded is the formation of cresolsulphonic acid from chloro- or bromo-toluenesulphouic acids, orcinol from bromocresol or dibromotoluene, catechol-4-sulphonic acid from sodium 1:2-dichlorobenzene-4-sulphonate, 3:5-dihydroxybenzoic acid from 3:5-dihalogenobenzoic acids, salicylaldehyde from *o*-chlorobenzaldehyde, *α*- and *β*-naphthols from the respective chloronaphthalenes, and alizarin from 1:2-dichloroanthraquinone.

CHEMICAL ABSTRACTS.

The Preparation of 2:4-Dinitrophenetole and 2:4:6-Trinitrophenetole. M. MARQUEYROL and SCOHY (*Bull. Soc. chim.*, 1920, [iv], **27**, 105—107).—2:4-Dinitrophenetole may readily be prepared by the action of aqueous sodium hydroxide on an alcoholic solution of 1-chloro-2:4-dinitrobenzene at 36°, gradually rising to 55°. If this phenetole is then nitrated in sulphuric acid solution at 30—40°, an excellent yield of 2:4:6-trinitrophenetole is obtained.

W. G.

The Synthesis of Aldehydes and Hydroxy-acids by means of Secondary *ααα*-Trichloro-alcohols. PIERRE HÉBERT (*Bull. Soc. chim.*, 1920, [iv], **27**, 45—55).—Bossneck's method for the preparation of aldehydes or hydroxy-acids by the action of potassium hydroxide ou *ααα*-trichloro-secondary alcohols (compare A., 1885, 976; 1886, 458) is shown to be generally applicable in the aliphatic, cyclic, aromatic, naphthalene, and aryl aliphatic series. The potassium hydroxide may be replaced by the hydroxides of sodium, calcium, magnesium, or barium, or advantageously by sodium carbonate. The trichloro-alcohols of the aliphatic series do not give such good yields as do the aromatic alcohols, where the ·CH(OH)· group is directly attached to a ring carbon atom. The activity in the aromatic series is diminished if this group is separated from the nucleus by one or more carbon atoms. The following new compounds are described.

By condensing magnesium *p*-bromophenyl bromide with anhydrous chloral, *β*-p-*bromophenyltrichloromethylcarbinol*,

$$C_6H_4Br\cdot CH(OH)\cdot CCl_3,$$

b. p. 183—187°/18 mm., is obtained, giving an *acetate*, m. p. 145—147°, and this on decomposition with sodium carbonate gives *p*-bromobenzaldehyde and *p*-bromophenylglycollic acid.

Magnesium benzyl bromide reacts with chloral to give *phenyltrichloroisopropyl alcohol*, $CH_2Ph\cdot CH(OH)\cdot CCl_3$, b. p. 158—160°/18 mm., giving an *acetate*, m. p. 110—111°.

o-4-Xylyltrichloromethylcarbinol is decomposed by sodium

carbonate, giving 3:4-dimethylbenzaldehyde and 3:4-*dimethylphenylglycollic acid*, $C_6H_3Me_2\cdot CH(OH)\cdot CO_2H$, m. p. 115—116°.
Ethyl a-naphthylglycollate, $C_{10}H_7\cdot CH(OH)\cdot CO_2Et$, has m. p. 68—69°. W. G.

Mercury Benzoate. ROBERT WOOD TERRY (*Midl. Drug. and Pharm. Rev.*, 1919, **53**, 222—225; from *Chem. Zentr.*, 1919, iii, 866).—A 1% solution of mercury benzoate is obtained by dissolving 2·715 parts of mercuric chloride and 2·880 parts of sodium benzoate in 442 parts of water, and filtering after a week.
H. W.

Abietic Acid. DAVID JOHANSSON (*Arkiv Kem. Min. Geol.*, 1917, **6**, No. 19).—Very little is known as to the derivatives and decomposition products of abietic acid. The author has therefore sought evidence of its unsaturation and of the presence in its molecule of the aromatic and hydroaromatic nuclei postulated by previous investigators (compare Easterfield and Bagley, T., 1904, 1238; Levy, A., 1913, i, 620). The acid, prepared from American colophony by Hunt and Pochin's process, had m. p. 168—173° (sintering at 155°), and in alcoholic solution $[\alpha]_D^{20}$ −28·6°. Both the Hübl-Waller and the Winkler iodine numbers increased with the duration of the determination, respective values of 102—171 and 150—357 being obtained. Since, approximately, the same values were obtained from the dihydro-derivative (below), and this behaviour was reproduced by the congener *d*-pimaric acid and its dihydro-derivative, it would appear that the unreduced acids contain at least two double bonds, which are not equivalent, or that substitution takes place. Halogenated compounds could not, however, be isolated. *Dihydroabietic acid*, $C_{20}H_{32}O_2$, m. p. 173—178° (sintering at 156°), was obtained by hydrogenation in ethereal solution in presence of platinum-black. Unlike abietic acid, it is unchanged after long exposure. Treated with chloroform and glacial acetic and sulphuric acids, it gives a reddish-violet colour, changing to yellowish-brown, whilst abietic acid gives a deep blue colour, which becomes brownish-green. From sulphonation experiments, a very small proportion of a mixture of acids was obtained. *Dinitroabietic acid*, $C_{20}H_{28}O_2(NO_2)_2$, produced by nitration with fuming acid below 10°, separates from acetone in needles, m. p. 178—184°, $[\alpha]_D^{20}$ +44·26°, which, on exposure to sunlight, turn red in a few seconds, and eventually brownish-green. The *sodium* salt, $C_{20}H_{27}O_2(NO_2)_2Na,1\frac{1}{2}H_2O$, needles, the *potassium* salt, and the *barium* salt, $[C_{20}H_{27}O_2(NO_2)_2]_2Ba,4H_2O$, yellowish-white needles, crystallise much better than those of abietic acid; the *silver* salt, $C_{20}H_{27}O_2(NO_2)_2Ag$, is a flocculent precipitate. In contrast with abietic acid, its dinitro-derivative is esterified by treatment with alcohol and hydrochloric acid. The *methyl* ester forms needles, m. p. 178—182°. The *ethyl* ester,

$$C_{19}H_{27}(NO_2)_2\cdot CO_2Et,$$

needles, m. p. 156—158°, is best prepared from the silver salt, and

is only hydrolysed by alkali with difficulty. Molecular compounds of the dinitro-derivative with, in some cases, four, and in others six, molecular proportions of naphthalene, anthracene, phenanthrene, and retene separate from alcohol in white needles, stable to light, which respectively melt at 110—117° (decomp.), 244—246°, 235—236°, and 234—238°. *Diamino-abietic acid dihydrochloride*, $C_{20}H_{28}O_2(NH_2,HCl)_2$, is a brown, amorphous powder, m. p. 280°, and very hygroscopic. A tarry product was obtained in an attempt to remove the amino-group by diazotisation. Crystallographic data are given for abietic, dihydroabietic, and dihydrodextropimaric acids. The presence of an aromatic or hydroaromatic nucleus in the molecule of abietic acid is regarded as now definitely determined. J. K.

The Action of Nitrites on some Imino-ethers. A. BERNTON (*Arkiv Kem. Min. Geol.*, 1918—1919, **7**, No. 13, 1—21).—The product of the action of nitrous acid on ethyl benzoyliminoacetate is not a nitroso-derivative (Haller, A., 1887, 826), but is identical with ethyl oximinobenzoylacetate (Perkin, T., 1885, **47**, 243). *Ethyl imino-oximinobenzoylacetate*, COPh·C(NOH)·C(NH)·OEt, leaflets, m. p. 112°, is obtained as the intermediate product when a cold solution of ethyl iminobenzoylacetate is added to a cold solution of sodium nitrite, and passes into ethyl oximinobenzoylacetate on warming or when treated with acids. Further, chloro-oximinoacetophenone, by treatment with potassium cyanide and hydrochloric acid, furnishes oximinobenzoylacetonitrile (E. v. Meyer, A., 1885, 582), which is converted by hydrochloric acid in alcoholic solution into the hydrochloride of ethyl imino-oximinobenzoylacetate. The *hydrochloride*, $C_{11}H_{13}O_3N_2Cl$, m. p. 114°, is precipitated by leading dry hydrogen chloride into its ethereal solution. It can also be similarly obtained from the product of the action of amyl nitrite on an ethereal solution of ethyl iminobenzoylacetate, whilst, by passing dry ammonia into a similar solution or a solution of ethyl imino-oximinobenzoylacetate in alcohol, *oximinobenzoylacetamidine*, $C_9H_9O_2N_3$, sulphur-yellow crystals, m. p. 227—229°, is produced. Its *hydrochloride*, $C_9H_{10}O_2N_3Cl$, is faintly yellow, and begins to lose hydrochloric acid at 200°. The *sulphate*, $C_9H_{11}O_5N_3S$, melts at 195°.

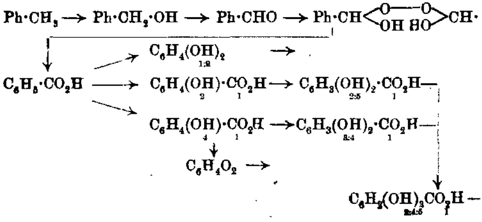
The action of nitrous acid on ethyl iminophenylacetate leads to the formation of ethyl phenylacetate and phenylacetamidine nitrite, $CH_2Ph·C(NH)·NH_2,HNO_2$ (Lossen, *Diss.*, Koenigsberg, 1890; Kammer, *ibid.*, 1893), m. p. 147°. This compound was further identified by the preparation of its acetate, m. p. 195°, and its nitrate, m. p. 166—167°, and its conversion into phenylacetamide by the action of sodium hydroxide.

In agreement with Knorr's view (A., 1917, i, 255) that the formation of amidines by the action of ammonia on the hydrochlorides of imino-esters is conditioned by ammonium chloride, it is shown that the nitrate of *p*-tolylacetamidine is produced by the action of ammonium nitrate on ethyl imino-*p*-tolylacetate. J. K.

Electrochemical Oxidation of Benzaldehyde and Benz Acid. FR. FICHTER and ELDOR UHL (*Helv. Chim. Acta.*, 1920, 22—39).—According to the literature, the anodic oxidation toluene and *p*-nitrotoluene at platinum electrodes appears to l only to the formation of benzaldehyde and *p*-nitrobenzyl alcc respectively; these results do not appear to harmonise with powerful oxidising action usually associated with anodic oxyg Since, also, Fichter and Stocker (A., 1914, i, 947) have found t quinone among the products of the electrolytic oxidation of tolu the whole question has been re-examined with particular refere to the substances formed in minor quantity.

The electrolytic oxidation of a suspension of benzaldehyde 2*N*-sulphuric acid at platinum anodes gave much unchan material and benzoic acid as the only isolable substances, but discrepancy between the amounts of original and final mate pointed to a further oxidation of the benzoic acid formed. Di experiment with the latter substance showed that it is actually c verted into catechol, quinol, 2:5-dihydroxybenzoic acid, and hydroxyquinolcarboxylic acid. The latter substances possibly (their origin to the intermediate production of *o*- and *p*-hydro benzoic acids, and, under the experimental conditions, salicylic a was found to yield quinolcarboxylic acid, whilst *p*-hydroxybenz acid gave protocatechuic acid. The production of quinolcarbox acid is also observed in the electrolytic oxidation of benzaldeh and toluene.

Measurements of potential with toluene, benzyl alcohol, be aldehyde, and benzoic acid, respectively, show a rapid and rema able increase of anodic polarisation in the case of the aldehyde; t same phenomenon is observed to a much smaller degree with ben alcohol and toluene, whilst with benzoic acid, anodic polarisatio very feeble; the results show that it is impossible so to cont electrolytic oxidation that only benzyl alcohol is produced, and a that benzoic acid can be further oxidised even in the presence of excess of toluene. The peculiar behaviour of benzaldehyde attributed to the formation of a peroxide, presumably eit dibenzylidene peroxide hydrate or dibenzylidene peroxide, si evidence of the production of the volatile benzoic peracid, $Ph{\cdot}CO_3$



could not be obtained. The electrolytic oxidation of toluene thus follows the lines of the scheme on the previous page. H. W.

A New Method of Synthesis of Indenic Ketones. A. Orékhoff (*Bull. Soc. chim.*, 1919, [iv], **25**, 597—598).—An application of the method previously described for the synthesis of indene derivatives (compare A., 1914, i, 265). When benzylidenedeoxybenzoin dibromide is heated at 140—145°, it loses two molecules of hydrogen bromide and gives diphenylindone, m. p. 151—152°; this yields a *phenylhydrazone*, m. p. 175—176°.
W. G.

Action of Cyanogen and its Haloids on Mixed Organomagnesium Derivatives. New Methods of Synthesis of Nitriles and Ketones. New Method of Introduction of a Halogen into an Organic Molecule. V. Grignard, E. Bellet, and Ch. Courtot (*Ann. Chim.*, 1919, [ix], **12**, 364—393. Compare A., 1916, i, 487).—The first part of the paper is a more detailed account of work already published (compare A., 1911, i, 292; 1912, i, 623; 1914. i, 391). By using 2 mols. of the magnesium alkyl or aryl haloid to 1 mol. of cyanogen chloride, a ketimine results which, when hydrolysed with water or dilute hydrochloric acid, gives the corresponding ketone (A., 1914, i, 391). In this way, the authors have prepared benzophenone, 4:4′-dimethylbenzophenone, 2:2′-*dimethylbenzophenone*, m. p. 72°, giving an *oxime*, m. p. 105°, αα-dinaphthyl ketone, 2:4-dimethylbenzophenone, and phenyl α-naphthyl ketone. W. G.

Derivatives of Naphthyl-β-ethylamine. Antonio Madinaveitia (*Bull. Soc. chim.*, 1919, [iv], **25**, 601—610; *Anal. Fis. Quim.*, 1918, **16**, 543—545).—The author has prepared a number of naphthalene derivatives having a side-chain with an amino-group in the β-position with the view of studying their action on the sympathetic nervous system in comparison with that of β-methylamino-α-phenylethane and its derivatives.

α-Chloro-β-bromo-α-methoxyethane when added to a solution of magnesium in bromobenzene and ether gives *β-bromo-α-methoxy-α-phenylethane*, b. p. 125—127°/15 mm., which when heated with methylamine in benzene solution at 100° for three hours gives *β-methylamino-α-methoxy-α-phenylethane*, b. p. 105—106°/22 mm., giving a *hydrochloride* and a *platinichloride*, m. p. 189° (decomp.). *β-Methylamino-α-methoxy-α-naphthylethane* is similarly prepared, with the intermediate formation of *β-bromo-α-methoxy-α-naphthylethane*, b. p. 185—190°/14 mm., and gives a *hydrochloride* and a *platinichloride*.

α-Naphthyl methyl ketone, when acted on by amyl nitrite in the presence of sodium ethoxide, gives *α-naphthyl nitrosomethyl ketone*, giving a *sodium* salt, and this nitroso-derivative, when reduced with stannous chloride and hydrochloric acid, yields *α-naphthyl aminomethyl ketone*, $C_{10}H_7{\cdot}CO{\cdot}CH_2{\cdot}NH_2$, giving a *hydrochloride*.

Similarly, 4-methoxy-α-naphthyl methyl ketone gives a *nitroso*-derivative, which on reduction yields *4-methoxy-α-naphthyl aminomethyl ketone*, isolated as its *hydrochloride*, which when heated in a sealed tube for four hours at 100° with fuming hydrochloric acid gives *4-hydroxy-α-naphthyl aminomethyl ketone*, isolated as its *hydrochloride*.

The vaso-constrictive action of these substances has been studied by Trendelenburg's method. It is shown that the introduction of a methoxy-group into the side-chain has little or no influence on the physiological action of the substance, but the replacement of the phenyl nucleus by a naphthyl nucleus has a very marked effect, increasing the vaso-constrictive action about forty times in the case of the substances studied. 4-Hydroxy-α-naphthyl aminomethyl ketone possesses a very marked vaso-constrictive action, which is much greater than that of the corresponding derivative without the hydroxyl group or than that of the corresponding derivative without the carbonyl group in the side-chain. W. G.

The Constitution of Dypnopinacone and its Derivatives. IV. The Luteo-dypnopinacones. MAURICE DELACRE (*Ann. Chim.*, 1919, [ix], **12**, 394—425. Compare A., 1914, i, 1068; 1916, i, 479; 1918, i, 539; this vol., i, 165).—A more detailed account of work already published (compare A., 1891, 456; 1896, i, 662).

W. G.

[Preparation of] *p*-Benzoquinone from Benzene. J. M. WEISS and C. R. DOWNS (U.S. Pat. 1318631).—A mixture of benzene and oxygen or air in the form of vapour or spray is passed over pumice impregnated with vanadium oxide and heated at 300—700°. *p*-Benzoquinone, maleic acid, and by-products are obtained, together with unchanged benzene. As substitutes for the catalyst, vanadium or vanadium compounds, molybdenum, tungsten, gold, ruthenium, cobalt, or the oxides of copper, manganese, cobalt, lead, chromium, antimony, cadmium, and thorium, may be used. The reaction may be carried out at pressures greater than, equal to, or less than atmospheric pressure. After removal of maleic acid by crystallisation or by solution in water, the remaining liquid products may be again passed over the catalyst to effect further oxidation, with the production of additional *p*-benzoquinone and maleic acid. CHEMICAL ABSTRACTS.

A Novel Degradation in the Anthraquinone Series. K. FRIES and E. AUFFENBERG (*Ber.*, 1920, **53**, [*B*], 23—28).—When the hydrochloride of 1-aminoanthraquinone is exhaustively chlorinated in glacial acetic acid, it yields 2:2:3:4:4-*pentachloro-1-keto-1:2:3:4-tetrahydroanthraquinone*, $C_6H_4<\begin{matrix}CO\cdot C\cdot CO-CCl_2\\CO\cdot C\cdot CCl_2\cdot CHCl\end{matrix}$, which crystallises in rhombic tablets, m. p. 166—168° (slight decomp.), and may be reduced by stannous chloride to 2:4-*dichloro-1-hydroxyanthraquinone*, slender, orange-coloured needles, m. p.

42°. The compound may also be reduced by boiling an acetic cid solution with ammonium chloride, the product being 2:3:4-richloro-1-*hydroxyanthraquinone*, which crystallises in orange eedles, m. p. 214°, forms sparingly soluble, brilliant red alkali alts, and is remarkably stable towards chlorine or concentrated itric and sulphuric acids.

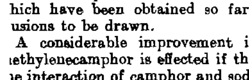
The pentachloro-derivative undergoes a novel hydrolysis when armed with concentrated sulphuric acid, the product being -2:3:4:6-*tetrachloro*-5-*hydroxybenzoylbenzoic acid*, formed by he rupture of the middle ring, according to the equation

$$C_{14}H_5O_3Cl_5 + H_2O = C_{14}H_6O_4Cl_4 + HCl.$$

t crystallises in minute druses, m. p. 277—278°, forms a sparingly oluble *sodium salt* and an *acetate*, m. p. 213°, and is hydrolysed y heating at a higher temperature with sulphuric acid to phthalic cid and 2:3:4:5-tetrachlorophenol. The same derivative of enzoylbenzoic acid is formed as a by-product when the original, rude chlorination product, containing ammonium chloride, is boiled ith acetic acid, but it is not given by the main product of this eaction, namely, the above trichlorohydroxyanthraquinone.

J. C. W.

Stereoisomeric Derivatives of Aminomethylenecamphor.
. HANS RUPE, MAX SEIBERTH, and WALTER KUSSMAUL (*Helv. him. Acta*, 1920, **3**, 50—70).—Aminomethylenecamphor and many f its derivatives are found to exist in two forms, characterised by ower melting point and generally greater solubility, and higher elting point and usually more sparing solubility; these are esignated β- and α-compounds respectively. In general, they are adily mutually transformable. Since a new asymmetric carbon tom is not developed during the formation of these substances, ptical isomerism is out of the question, and it appears certain that stances of *cis-trans*-isomerism (annexed formula) are being dealt with, although direct experimental evidence on this point is lacking. The optical investigation of these substances promises results of considerable interest, since but few optically



ctive *cis-trans*-isomerides have been examined; the sparing solubility of the products at the ordinary temperature and the ease ith which they undergo transformation when the temperature is aised have prevented an extended examination, and the results hich have been obtained so far do not allow any general conusions to be drawn.

A considerable improvement in the preparation of hydroxyethylenecamphor is effected if the sodium camphor is prepared by e interaction of camphor and sodamide in benzene solution; under ese conditions, the formation of borneol is avoided, and any nattacked camphor can be recovered.

α-Aminomethylenecamphor is conveniently prepared by heating

hydroxymethylenecamphor with saturated aqueous ammonia under pressure at 100°; it forms colourless, shining leaflets, m. p. 156°, D_4^{20} 0·8176, $[\alpha]_C^{20}$ + 191·37°, $[\alpha]_D^{20}$ + 257·32°, $[\alpha]_{Hg}^{20}$ + 323·41°, $[\alpha]_F^{20}$ + 477·19°, $[\alpha]_F/[\alpha]_C$ 2·48 in alcoholic solution. When distilled under diminished pressure, it is quantitatively converted into the β-*form*, m. p. 103—104°, D_4^{20} 0·8159, $[\alpha]_C^{20}$ +236·57°, $[\alpha]_D^{20}$ +313·76°, $[\alpha]_E^{20}$ + 388·23°, $[\alpha]_F^{20}$ 553·99°, $[\alpha]_F/[\alpha]_C$ 2·34. The latter is very labile, but can be preserved unchanged in substance, even if exposed to sunlight; it is converted into the α-form if its solution in alcohol or benzene is evaporated, when the benzene solution is exposed to sunlight, or when the alcoholic solution is boiled.

α-*Benzoylaminomethylenecamphor* is the sole product of the action of benzamide on hydroxymethylenecamphor in glacial acetic acid solution, and is formed, together with the β-*isomeride*, by the benzoylation of aminomethylenecamphor in pyridine solution; it forms slender, colourless needles, m. p. 208°, D_4^{20} 0·9838, $[\alpha]_C^{20}$ + 164·28°, $[\alpha]_D^{20}$ + 219·29°, $[\alpha]_{Hg}^{20}$ + 273·15°, $[\alpha]$ + 393·06°, $[\alpha]_F/[\alpha]_C$ 2·39 in pyridine solution. The β-modification crystallises in monoclinic prisms [$a:b:c$=0·96402:1:1·05011, β=110°40′], m.p. 112°, D_4^{20} 0·9835, $[\alpha]_C^{20}$ + 166·44°, $[\alpha]_D^{20}$ + 228·29°, $[\alpha]_{Hg}^{20}$ + 292·67°, $[\alpha]_F^{20}$ + 453·11°, $[\alpha]_F/[\alpha]_C$ 2·72; it is converted into the α-variety when its solution in light petroleum is exposed to ultra-violet light, but not by treatment with hydrogen chloride in alcoholic or light petroleum solution. The reverse transformation is effected by boiling a solution of the α-form in pyridine.

α- and β-p-*Nitroanilinomethylenecamphor*,

$$C_8H_{14}<\begin{matrix}C:CH\cdot NH\cdot C_6H_4\cdot NO_2\\ CO\end{matrix},$$

are simultaneously formed by the action of *p*-nitroaniline on hydroxymethylenecamphor in glacial acetic acid solution, and are separated by taking advantage of the greater solubility of the β-isomeride in cold benzene. The α-form crystallises in canary-yellow leaflets, m. p. 180—181°, and slowly passes into the β-isomeride at the ordinary temperature, rapidly at 200°; the β-isomeride forms orange-yellow needles with a violet reflex, m. p. 151—152°, and is converted into the α-form when its solution in boiling alcohol is exposed to direct sunlight.

p-*Phenylenediaminodimethylenecamphor*,

$$C_8H_{14}<\begin{matrix}C:CH\cdot NH\cdot C_6H_4\cdot NH\cdot CH:C\\ CO \qquad\qquad\qquad\qquad\qquad\qquad CO\end{matrix}>C_8H_{14},$$

pale yellowish-green, microscopic needles, m. p. 276—277°, appears to be the sole product of the action of *p*-phenylenediamine on hydroxymethylenecamphor; it could only be obtained in one form.

p-*Acetylaminoanilinomethylenecamphor*,

$$C_8H_{14}<\begin{matrix}C:CH\cdot NH\cdot C_6H_4\cdot NHAc\\ CO\end{matrix},$$

forms pale yellowish-green leaflets, m. p. 226—227°, and exists in one form only. p-*Aminoanilinomethylenecamphor* could not be obtained by the reduction of the corresponding nitro-compound by iron and acetic acid; although reduction appears to occur, the amino-derivative is immediately hydrolysed, and condensation then occurs between the *p*-phenylenediamine and hydroxymethylenecamphor, which are thus formed with the ultimate production of *p*-phenylenediaminodimethylenecamphor; reduction could not be effected with ammonium sulphide, whilst with sodium sulphide either form of the nitro-compound yields the same amino-derivative in poor yield. The pure amine, m. p. 163°, is, however, obtained by the action of ethyl-alcoholic potassium hydroxide on the corresponding acetyl derivative. The *hydrochloride* is sparingly soluble in water and cannot be diazotised.

p-*Phenetidinomethylenecamphor* (β-form, coarse plates and prisms, m. p. 111—112°; α-form, pale yellowish-green leaflets, m. p. 166—167°) is prepared by the action of *p*-phenetidine on hydroxymethylenecamphor in alcoholic solution, and is separated into its isomerides by fractional crystallisation from benzene. The β-variety is very labile, and is converted into the α-variety when attempts are made to recrystallise it from alcohol; it has not been found possible to effect the reverse transformation. H. W.

Stereoisomeric Derivatives of Aminomethylenecamphor. II. HANS RUPE, MAX SEIBERTH, and WALTER KUSSMAUL (*Helv. Chim. Acta*, 1920, **3**, 71—89).—A continuation of the work described in the preceding abstract.

Diethylaminomethylenecamphor, $C_8H_{14}<\begin{matrix}C:CH\cdot NEt_2\\CO\end{matrix}$, is obtained as a pale yellow, viscous oil, b. p. 175—175·5°/11 mm., which solidifies when cooled to a mass of transparent plates, m. p. 20—22°, by the action of diethylamine on hydroxymethylenecamphor or chloromethylenecamphor. The *hydrochloride* is slowly decomposed in aqueous solution, yielding hydroxymethylenecamphor and diethylamine hydrochloride. *Piperidinomethylenecamphor* is a pale yellow, viscous oil, b. p. 203—204°/11 mm., m. p. 60° after softening at 58°; the *hydrochloride*, slender needles, suffers first dissociation and then hydrolysis in aqueous solution. *Tetrahydroquinolinomethylenecamphor* forms coarse, transparent prisms, m. p. 109°. *Carbamidomethylenecamphor*, $C_8H_{14}<\begin{matrix}C:CH\cdot NH\cdot CO\cdot NH_2\\CO\end{matrix}$, prepared by melting the components together or by condensation in glacial acetic acid solution, crystallises in needles, m. p. 197°; a second modification, which does not melt below 280°, possibly exists. β-*Ethylurethanomethylenecamphor* is exclusively obtained when its components are heated together at 110°, and forms a colourless, odourless, highly refractive oil, which does not solidify in a mixture of ice and salt, and rapidly becomes yellow or red when preserved; it has b. p. 178—179°/10 mm., D_4^{20} 0·9835, $[\alpha]_C^{20}$ +145·93°, $[\alpha]_D^{20}$ +197·17°, $[\alpha]_{Hg}^{20}$ +247·62°, $[\alpha]_F^{20}$ +366·69°, $[\alpha]_F/[\alpha]_C$

2·51 in pyridine solution. When, however, the components are mixed in glacial acetic acid solution, the α-variety is mainly formed at the ordinary temperature, but the reaction is very incomplete, whilst at a higher temperature reaction proceeds quantitatively, but yields more of the β-variety. The *α-isomeride* forms colourless, many-sided crystals, m. p. 162°, D_4^{20} 0·98352, $[\alpha]_C^{20}$ +149·42°, $[\alpha]_D^{20}$ +198·52°, $[\alpha]_{Hg}^{20}$ +245·11°, $[\alpha]_F^{20}$ +347·35°, $[\alpha]_F/[\alpha]_C$ 2·32. Transformation of the β- into the α-variety can be effected by hydrogen bromide, hydrogen chloride, concentrated sulphuric acid, nitrous fumes, iodine in ethereal solution, by exposure to direct sunlight, and by preservation in the dark. The reverse action is effected by boiling a solution of the α-variety in glacial acetic acid with exclusion of light.

The two forms of *ethyl methylenecamphor-p-aminobenzoate* are simultaneously formed by the condensation of the components in glacial acetic acid solution, and are separated with the aid of light petroleum; the α-variety crystallises in minute needles, m. p. 176°, whilst the β-form has m. p. 105°. The former modification is exclusively formed when a mixture of the components is gently heated; it appears to be exceptionally stable, but undergoes partial transformation when its solution in formic acid is boiled during a protracted period in direct sunlight and in the presence of iodine.

The *methylenecamphoranthranilic acids* are simultaneously formed from hydroxymethylenecamphor and anthranilic acid in glacial acetic acid solution, and can be separated to some extent mechanically, owing to the difference in their crystalline forms. Separation by means of solvents is impracticable, owing to their very similar solubilities. Isolation of the β-variety is best effected by boiling the mixture of isomerides with benzene, when the α-variety passes into the β-form, almost colourless needles, which rapidly become brown, and have m. p. 112° and 176° after resolidifying. The α-variety is conveniently obtained by boiling a solution of the β-form in toluene, and forms pale brown, many-sided crystals, m. p. 176°; the latter isomeride is exclusively formed when the components are heated together, the result being attributable to the high temperature of the reaction. Attempts to convert the methylenecamphoranthranilic acids into indole or indigo-derivatives were unsuccessful. Acetic anhydride, however, converts the β-derivative into *methylenecamphor-N-acetylanthranilic acid*, $C_8H_{14}<\begin{matrix}C:CH\cdot NAc\cdot C_6H_4\cdot CO_2H\\ |\\ CO\end{matrix}$, colourless, shining needles united in clusters, m. p. 185°, to an intensely green liquid, which gradually becomes reddish-brown. Either variety is transformed by phosphoryl chloride into the *β-lactam* of methylenecamphoranthranilic acid, $C_6H_4<\begin{matrix}N\cdot CH:C\\ | \quad\quad |\\ CO \quad OC\end{matrix}>C_8H_{14}$, colourless crystals, which immediately become discoloured on exposure to air and have m. p. 165°. The substance is converted by boiling water into methylenecamphoranthranilic acid, and by cold alkali into a mixture of the sodium salts of the two forms of the acid.

Methylenecamphor-p-aminophenylarsinic acid,

$$C_8H_{14}<\begin{matrix}C:CH\cdot NH\cdot C_6H_4\cdot AsO_3H_2\\ CO\end{matrix},$$

is best obtained as *sodium* salt by heating hydroxymethylenecamphor with atoxyl at 110°; it forms slender, colourless needles, which decompose at 220° and melt indistinctly at 250°; anilinomethylenecamphor, m. p. 168—170°, and a substance, $C_{27}H_{42}O_2$, slender, yellow needles, m. p. 188°, are formed as by-products during the condensation. H. W.

Transpositions in the Camphene Series. G. LANGLOIS (*Ann. Chim.*, 1919, [ix], **12**, 265—363. Compare this vol., i, 171). —By the direct bromination of camphene in anhydrous ether, ω-bromocamphene, b. p. 115—120°/15 mm., 225—226°/760 mm., D^{15} 1·265, $[\alpha]_D$ +68·85°, is obtained, its constitution being proved by its behaviour on oxidation either by nitrous vapour or by potassium permanganate, camphenylone being the product in either case. In the preparation of a magnesium derivative from bromocamphene, some *dehydrodicamphene*, $C_{10}H_{15}\cdot C_{10}H_{15}$, m. p. 181°, is obtained. The magnesium derivative when acted on by carbon dioxide gives an *acid*, $C_{10}H_{15}\cdot CO_2H$, m. p. 124—125°, which on oxidation also gives camphenylone and oxalic acid. ω-Bromocamphene is stable towards Beckmann's oxidising mixture, and with hydrogen bromide yields 2-ω-dibromocamphane, the latter change being reversible. Attempts to replace the bromine in bromocamphene with a phenyl group by means of magnesium phenyl bromide were not very successful, whilst with magnesium methyl iodide the product was cymene. On chlorination in ether, bromocamphene gives *dichlorobromocamphene*, $C_{10}H_{15}Cl_2Br$, m. p. 74°. Hydrogen chloride in the cold is without action on bromocamphene, but when passed into an acetic acid solution at 100° it yields dibromocamphane. As compared with camphene, bromocamphene only undergoes very slow acetylation, and the product is not characterised.

By carefully restricted chlorination of camphene, a certain amount of chlorocamphene, b. p. 95—98°/15 mm., D^{15} 1·016—1·017, $[\alpha]_D$ +37°, is obtained, which is not acted on by any hydrogen chloride or by Beckmann's oxidising agent. With potassium permanganate, it is oxidised to camphenylone. With hydrogen bromide, it gives *ω-chloro-2-bromocamphane*, m. p. 103°, and on further chlorination it gives trichlorocamphene, m. p. 104°. On bromination it gives *chlorodibromocamphene*, $C_{10}H_{13}ClBr_2$, m. p. 64—65°.

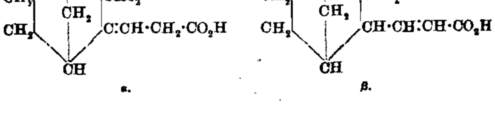
When camphene is heated on an oil-bath for two days with a mixture of trioxymethylene and acetic acid, it gives an *acetate*, $C_{11}H_{17}\cdot CO_2\cdot CH_3$, b. p. 130—135°/20 mm., which on hydrolysis gives a primary alcohol, *camphenylidene-6-ethanol*,

$$C_9H_{14}:CH\cdot CH_2\cdot OH,$$

b. p. 125—126°/8 mm., 135°/17 mm., 234—238°/760 mm., D^{15} 0·987—0·988, $[\alpha]_D$ +45°, which is best purified through its *hydrogen phthalate*, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{11}H_{17}$, m. p. 124—125°. If the alcohol is subjected to prolonged heating with alcoholic potassium

hydroxide, it gives an *ether*, $O(CH_2{\cdot}CH{:}C_9H_{14})_2$, b. p. 235—240°/25 mm., D^{20} 0·983. The alcohol, $C_{11}H_{17}{\cdot}OH$, when oxidised with potassium permanganate in the presence of aqueous sodium carbonate, gives camphenylone, hydroxycamphenylanic acid, and oxalic acid. In the presence of sodium hydroxide, the products of oxidation are camphenylone, camphenecamphoric acid, and oxalic acid. By a similar study of the oxidation of camphene, it is shown that the endocyclic transposition is not due to the permanganate, but rather to the isomerising action of the free alkali used in excess. Certain derivatives of camphenylidene-6-ethanol have been prepared. It gives a *diphenylurethane*, difficult to purify, and a *pyruvate*, b. p. 150—155°/10 mm., giving a *semicarbazone*, m. p. 167°. The ether, $(C_{11}H_{17})_2O$, when oxidised by sodium dichromate and sulphuric acid, gives first an aldehyde, and then camphenylidene-ethanoic acid.

A *chloride*, $C_{11}H_{17}Cl$, corresponding with camphenylidene-6-ethanol, may be obtained either by the action of hydrogen chloride on the alcohol in toluene solution at 140—150°, or by the action of phosphorus pentachloride either on the alcohol or the corresponding ether. This chloride has b. p. 100—102°/6 mm., 110°/15 mm., D^{15} 1·020, $[\alpha]_D$ +27·38°. On oxidation with potassium permanganate, it yields camphenylone. Unlike ω-chlorocamphene, it is oxidised by sodium dichromate and sulphuric acid, giving first an aldehyde and then camphenylideneacetic acid. The chloride is quite stable towards either hydrogen chloride or hydrogen bromide, undergoing no transposition. Further, it is not reduced by sodium in absolute alcohol, but under these conditions simply gives an *ethyl ether*, $C_{10}H_{17}{\cdot}OEt$, b. p. 125—130°/8 mm., 230°/760 mm. This ether, when oxidised by the chromic acid mixture gives camphenylideneacetic acid. If the reduction of the chloride is carried out by zinc and hydrochloric acid, the product is *ω-methylcamphene*, b. p. 178°, D^{15} 0·884, $[\alpha]_D$ +4·28°. The chloride, $C_{11}H_{17}Cl$, when acted on by sodium or magnesium in anhydrous ether, gives a *terpenic hydrocarbon*, $C_{11}H_{17}{\cdot}C_{11}H_{17}$, b. p. 210°/25 mm., D^{15} 0·952, $[\alpha]_D$ +67·30°, which is remarkably stable towards aqueous potassium permanganate. By the action of sodium ethoxide, the chloride yields the corresponding ether, $(C_{11}H_{17})_2O$, described above. With sodium cyanide, the chloride yields the *nitrile*, $C_{11}H_{17}{\cdot}CN$, b. p. 140°/12 mm., D^{15} 0·959, D^{20} 0·963, $[\alpha]_D$ +61·20°, which is readily oxidised to camphenylone, and on hydrolysis gives the corresponding *acid*, $C_{11}H_{17}{\cdot}CO_2H$, m. p. 100°,



α. β.

b. p. 185°/24 mm., $[\alpha]_D$ +41·16°. From its behaviour on oxidation, it is suggested that this acid is really a mixture of two α- and β-isomerides (see formulæ on previous page). When camphenylidene-6-ethanol is oxidised by Beckmann's mixture in the cold, it yields *camphenylidene-6-acetaldehyde*, C_9H_{14}:CH·CHO, b. p. 130°/12 mm., 124°/8 mm., D^{15} 1·002, $[\alpha]_D$ +72·58°, which gives a sodium bisulphite *compound*, a *semicarbazone*, m. p. 233°, and an *oxime*, b. p. 160°/15 mm. The oxime gives a *hydrochloride*, and on dehydration yields *camphenylideneacetonitrile*, C_9H_{14}:CH·CN, b. p. 132°/6 mm., 140°/10 mm., D^{15} 0·987, D^{20} 0·983, $[\alpha]_D$ +110°, which when boiled with alcoholic potassium hydroxide gives the corresponding *amide*, $C_{10}H_{15}$·CO·NH_2, m. p. 192°. This amide is very stable, and is not hydrolysed by sulphuric acid. Camphenylideneacetaldehyde gives a *diacetate*, C_9H_{14}:CH·CH(CO_2Me)$_2$, m. p. 54—55°.

If the oxidation of camphenylidene-6-ethanol with Beckmann's mixture is pushed further, the product is *camphenylideneacetic acid*, m. p. 124—125°, b. p. 181°/19 mm., the same acid being obtained by the action of carbon dioxide on the magnesium derivative of ω-bromocamphene. It gives an *ethyl* ester, b. p. 150°/22 mm., D^{20} 1·008, and an *acid chloride*, b. p. 145°/15 mm., which by the action of ammonia is converted into the amide, m. p. 192° (see above). When heated on an oil-bath for several hours, camphenylideneacetic acid loses carbon dioxide and gives a *camphene*, m. p. 45—46°, b. p. 158—160°, which on oxidation yields camphor. On oxidation with potassium permanganate, the acid yields camphenylone, and on reduction with sodium in amyl alcohol it gives *iso*camphanecarboxylic acid, which when oxidised gives r-*camphenylanic acid*, m. p. 75—76°.

ω-Methylcamphene may be obtained by the reduction of camphenylideneacetaldehyde by zinc and hydrochloric acid, its constitution being shown by its behaviour on oxidation with potassium permanganate, when it yields camphenylone, oxalic acid, and camphenecamphoric acid. It is not oxidised by sodium dichromate and sulphuric acid, or by hydrogen chloride, but with hydrogen bromide it gives a *hydrobromide*, $C_{11}H_{19}$Br, b. p. 108—110°/17 mm., D^{15} 1·175.

Camphenylideneacetaldehyde is capable of condensing with ketones. Thus with acetone it yields the *ketone*,

C_9H_{14}:CH·CH:CH·COMe,

b. p. 160°/12 mm., D^{15} 0·980, giving a *semicarbazone*, m. p. 220—221°. With methyl ethyl ketone the aldehyde gives the *ketone*, C_9H_{14}:CH·CH:CH·COEt, b. p. 172—175°/12 mm., D^{15} 0·968, giving a *semicarbazone*, m. p. 209—210°. Owing to the presence of three conjugated double linkings, neither of these ketones is oxidised by chromic acid mixture, and the first-named is not acted on by hypochlorites. Camphenylideneacetaldehyde also reacts with magnesium alkyl haloids of low molecular weight to give unstable secondary alcohols, which, when distilled in a vacuum, give *diethylenic hydrocarbons*. Thus, with magnesium methyl

iodide, the final product is *camphenylidenepropylene*,

$C_9H_{14}\!:\!CH\cdot CH\!:\!CH_2$,

b. p. 85—90°/10 mm., 203—205°/760 mm., D^{15} 0·921, D^{20} 0·917 $[\alpha]_D$ +76·39°. With magnesium ethyl bromide the product is *camphenylidenebutylene*, $C_9H_{14}\!:\!CH\cdot CH\!:\!CHMe$, b. p. 95—97°/12 mm. and 230—232°/760 mm., D^{15} 0·919, $[\alpha]_D$ +70°. With magnesium propyl bromide the product is *camphenylidenepentene* $C_9H_{14}\!:\!CH\cdot CH\!:\!CHEt$, b. p. 110—120°/15 mm. and 238—240°/760 mm., D^{15} 0·905, $[\alpha]_D$ +80°, and with magnesium butyl bromide the product is *camphenylidenehexene*,

$C_9H_{14}\!:\!CH\cdot CH\!:\!CHPr$,

b. p. 140°/10 mm. and 255°/760 mm., D^{15} 0·900, $[\alpha]_D$ +73·5°. All these diethylenic hydrocarbons when oxidised with chromic acid mixture give the original aldehyde or camphenylideneacetic acid. They also undergo spontaneous oxidation, giving camphenylideneacetaldehyde and formaldehyde, acetaldehyde, propaldehyde, and butaldehyde respectively. W. G.

Chemistry of the Terpenes. XIX. Synthesis of a *m*-Menthadiene from *m-iso*Cymene. George Gerald Henderson and Thomas Frederick Smeaton (T., 1920, **117**, 144—149).

Occurrence of the Terpene Terpinene in the Oil of Eucalyptus megacarpa. Henry G. Smith (*J. Proc. Roy. Soc., N.S. Wales*, 1918, **52**, 529—533).—The oil of *Eucalyptus megacarpa* contains pinene, limonene, and dipentene, about 30% of cineole, and possibly as much as 10% of terpinene. The latter was detected in the fraction boiling from 170—190° by the formation of its nitrosite, m. p. 155°, and by its rapid oxidation in the cold with Beckmann's chromic acid mixture, as evidenced by the increased optical rotation of the residual oil (consisting mainly of limonene) after the removal of the inactive terpinene.

G. F. M.

The Vulcanisation of Caoutchouc with Agents other than Sulphur. Henry P. Stevens (*J. Soc. Chem. Ind.*, 1917, **35**, 107).—Vulcanisation of caoutchouc with from 1 to 4% of dinitrobenzene or trinitrobenzene at 140° is possible in the additional presence of a considerable proportion (for example, 8 to 30%) of lead oxide or magnesium oxide; the trinitro-compound is more effective than its dinitro-analogue, whilst with nitrobenzene itself satisfactory results are not obtainable. The nitro-compound enters almost entirely into combination with the caoutchouc, and is not removable by acetone. The products possess poor mechanical qualities relative to caoutchouc vulcanised in the ordinary way with sulphur. Benzoyl peroxide also effects vulcanisation, and in this case no third substance is necessary; from 4 to 6% of the peroxide is required, and a vulcanisation period of ten to fifteen minutes at 130—135°. The products are weak and have a remarkably pale colour. [See also Bunschoten, A., 1918, i, 503; Ostromisslenski, A., 1916, i, 278.]

D. F. T.

The Nature of Vulcanisation. I. The Combination of Rubber with Sulphur. II. The Action of Solvents on Vulcanised Rubber. H. P. STEVENS (*J. Soc. Chem. Ind.*, 1919, **38**, 192—196T).—The results on which Harries and Fonrobert (A., 1916, i, 659, 733) base their opinion that vulcanisation of caoutchouc is essentially a physical process, and may occur without any appreciable combination with sulphur, are probably explained by unsuitable conditions of experiment. Under similar conditions, but with the additional precaution of vulcanising the mixture of caoutchouc and sulphur in thin sheets, so as to ensure greater uniformity of heating, and consequently of vulcanisation, the author obtained a product which, after exhaustive extraction with acetone, retained more than 1% of combined sulphur. It is therefore not possible to effect ordinary vulcanisation without the concurrent fixation of an appreciable proportion of sulphur. With an increasing proportion of combined sulphur, caoutchouc becomes less and less soluble in solvents such as benzene; freshly vulcanised samples containing 0·27% and 0·39% of combined sulphur could be dissolved in benzene, whereas 0·45% prevented solution; after storage for three months, none of these samples would pass completely into solution. The extract obtained on treating more highly vulcanised caoutchouc with hot benzene contains the same proportion of combined sulphur as the undissolved residue.

D. F. T.

Autoxidation of Colophony. LUDWIG PAUL (*Kolloid Zeitsch.*, 1919, **25**, 241—246).—The constituents of colophony are investigated, and some of the products examined and characterised. When a solution of colophony in alkali is treated with hydrochloric acid, a voluminous precipitate of γ-pinic acid is obtained; this substance has m. p. 75—76°, which in eight months rises to about 88°. α-Pinic acid has a constant m. p. 81—83°, and shows a tendency to form liquid crystals. It is soluble in water and petroleum, as also is γ-pinic acid. β-Pinic acid melts at 98—100° (compare A., 1918, i, 411). J. F. S.

Compounds of High Molecular Weight. I. Synthesis of some Acylglucosides of High Molecular Weight. SVEN ODÉN (*Arkiv Kem. Min. Geol.*, 1917, **6**, No. 18).—Almost all known organic compounds of high molecular weight are natural products of indefinite constitution and extremely difficult to purify, circumstances which are great obstacles to the study of their physico-chemical properties. The author has now synthesised a series of esters of 2:4:6-tribromophenol-*d*-glucoside with a view to a study of the variation of their properties with molecular weight. The esters were prepared by E. Fischer's process, for which the most suitable conditions in this case consist in treating a suspension of the finely divided glucoside in dry chloroform with excess (about one-third) of the acid chloride and quinoline at about 50°. The product was usually isolated by precipitation from the solution by

alcohol, and purified by repetition of the treatment, the brom content furnishing an effective criterion of purity. The consta of melting point of the products renders it improbable that use of quinoline caused any stereoisomeric change during the re tion. All the products were stable, indifferent substances, slightly lævorotatory. With the exception of the tetrapropion the tetrabenzoate, and the tetra-*p*-bromobenzoate, which are cryst line, they were amorphous substances resembling stearin or f and in their aspect and solubility relationships lipoid in charact It is noteworthy that the tetrabenzoate exists in two interc vertible forms, an amorphous form, m. p. 94°, and a crystalli m. p. 147°, the difference in m. p. being apparently conditio by the variation in granular size (compare Pawlov, A., 19 ii, 1033).

The following derivatives of 2:4:6-tribromophenol-*d*-glucos are described: the *tetra-acetate*, $C_{20}H_{21}O_{10}Br_3$, needle-sha crystals, m. p. 195—196°; the *tetrapropionate*, $C_{24}H_{29}O_{10}$I prisms, m. p. 89·5°; the *tetralaurate*, $C_{60}H_{101}O_{10}Br_3$, resembling m. p. 48—49°; the *tetramyristate*, $C_{68}H_{117}O_{10}Br_3$, m. p. 56—5 the *tetrapalmitate*, $C_{76}H_{133}O_{10}Br_3$, resembling stearin, m. 61—62°; the *tetrastearate*, $C_{84}H_{149}O_{10}Br_3$, resembling stearin, m. 70—71°, in tetrachloroethane solution, $[\alpha]_D^{20}$ −3·6°; the *tet hexabromostearate*, $C_{84}H_{125}O_{10}Br_{27}$, fairly hard, m. p. 152°; *tetracerotate*, $C_{116}H_{213}O_{10}Br_3$, solid, m. p. 80—81°; the *tet benzoate*, $C_{40}H_{29}O_{10}Br_3$, m. p. as above; the *tetra*-p-*bromobenzoa* $C_{40}H_{25}O_{10}Br_7$, m. p. 115° amorphous, 214° crystalline (aggrega of needle-shaped crystals); the *tri-β-naphthoate*, $C_{45}H_{31}O_9Br_3$, m. 175°; the *tetra-β-naphthoate*, $C_{56}H_{37}O_{10}Br_3$, m. p. 218°.

In addition, the following were prepared from α-methyl glucoside: the *tripalmitate*, $C_{55}H_{104}O_9$, amorphous, m. p. 77°; t *tristearate*, $C_{61}H_{108}O_9$, amorphous, m. p. 82°; the *tetrasteara* $C_{79}H_{150}O_{10}$, amorphous, m. p. 68°; the *tetra*-p-*bromobenzoa* $C_{35}H_{26}O_{10}Br_4$, needles, m. p. 148°. J. K.

Compounds of High Molecular Weight. II. Some Ac Derivatives of Natural Glucosides of High Molecular Weig SVEN ODÉN (*Arkiv Kem. Min. Geol.*, 1918—1919, 7, No. 1—22).—The method of acylation previously described (see previc abstract) gives good results when applied to natural glucosides, a has the advantage over older methods of giving completely acylat products. In several cases the products were crystalline, with sharp melting point, but the granular size was again observed have a distinct influence on the melting point; in all cases this w depressed by precipitation of the amorphous or microcrystalli form by alcohol from a solution of the crystalline form in chlo form. The chlorides of β-naphthalene- and α-bromocamphor sulphonic acids were also used, this being the first occasion on whi sulpho-derivatives of members of the sugar group have been p pared. In these cases, however, a temperature above 50° w necessary for the condensation, the reaction proceeded less smooth

the resulting compounds were impure, and the yields only about 30%. The products were very friable, and appeared under the microscope as small, strongly refractive, glassy spheres. In the impure condition, they are not dissimilar from the oxidation products of sulphite liquors. The following derivatives are described.

Salicin:—*pentacinnamate*, $C_{58}H_{48}O_{12}$, needles, m. p. 173°, $[\alpha]_D^{19}$ +46·5°, *pentaphenylpropionate*, $C_{58}H_{58}O_{12}$, long needles, m. p. 58° $[\alpha]_D^{18}$ −3·5°, and *penta*-p-*bromobenzoate*, $C_{48}H_{33}O_{12}Br_5$, needles, m. p. 158°, $[\alpha]_D^{19}$ +30·2°.

Helicin:—*tetracinnamate*, $C_{49}H_{40}O_{11}$, prisms, m. p. 176°, $[\alpha]_D^{18}$ +77·3° (p-*bromophenylhydrazone*, $C_{55}H_{45}O_{10}N_2Br$, amorphous, m. p. 118—120°, decomp.), *tetrapalmitate*, $C_{77}H_{136}O_{11}$, amorphous, m. p. 68° (p-*bromophenylhydrazone*, $C_{83}H_{141}O_{10}N_2Br$, amorphous, m. p. ca. 45°).

Coniferin:—*pentacinnamate*, $C_{61}H_{52}O_{13}$, amorphous, m. p. ca 145°, and *tetrastearate*, $C_{88}H_{158}O_{12}$, amorphous, m. p. 69—70°.

Amygdalin:—*heptabenzoate*, $C_{69}H_{55}O_{18}N$, small needles, m. p. 218°, $[\alpha]_D^{18}$ −10·5°, *hepta*-p-*chlorobenzoate*, $C_{69}H_{48}O_{18}NCl_7$, crystals, m. p. 234°, slightly lævorotatory, *hepta*-p-*bromobenzoate*,

$$C_{69}H_{48}O_{18}NBr_7,$$

needles, m. p. 229°, *hepta-anisate*, $C_{76}H_{69}O_{25}N$, amorphous, m. p. 117—119°, $[\alpha]_D^{20}$ +13·2°, and *heptastearate*, $C_{146}H_{265}O_{18}N$, amorphous, m. p. 92°, $[\alpha]_D^{18·5}$ −8·40°.

Phloridzin:—*hepta*-p-*bromobenzoate*, $C_{70}H_{45}O_{17}Br_7$, amorphous, m. p. 130—132°, $[\alpha]_D^{19}$ +19·5°, and *heptapalmitate*, $C_{133}H_{234}O_{17}$, amorphous, m. p. 51°, $[\alpha]_D^{18·5}$ −9·55°.

a-Methyl-d-*glucoside*:—*tetra-β-naphthalenesulphonate*,

$$C_{47}H_{35}O_{14}S_4,$$

snow-white powder, m. p. 147°, *tetra-a-bromocamphor-π-sulphonate*, $C_{47}H_{66}O_{18}Br_4S_4$, glassy spheres, m. p. 150°, $[\alpha]_D$ +128°, and *tetrapalmitate*, $C_{71}H_{134}O_{10}$, needles, m. p. 69°, $[\alpha]_D^{18}$ +46·9°.

2 : 4 : 6-*Tribromophenol*-d-*glucoside*:—*tetra-a-bromocamphor-π-sulphonate*, $C_{52}H_{65}O_{18}Br_7S_4$, amorphous, m. p. 181°, $[\alpha]_D^{20}$ +75·1°.

All optical data refer to solutions in chloroform. J. K.

Compounds of High Molecular Weight. III. Derivatives of Raffinose and of some other Sugar Derivatives of High Molecular Weight. SVEN ODÉN (*Arkiv Kem. Min. Geol.*, 1918—1919, 7, No. 15, 23—38).—The eleven hydroxyl groups of raffinose render this compound a very suitable starting point for the synthesis of derivatives of high molecular weight. The method of acylation already described was successfully applied in this case, and gave completely acylated products (contrast Stollé, A., 1901, i, 189); but the reaction took place more slowly, and some material was always recovered unchanged; sulphonyl chlorides react still less readily than those of carboxylic acids. The products were all amorphous and definitely uniform, except possibly the hendecahexabromostearate. Amorphous derivatives were also obtained from saccharose, but mannitol and dulcitol furnished crystalline products. From inositol, only the hexa-*p*-bromobenzoate could be obtained. The following derivatives are described.

Raffinose:—hendecabenzoate, $C_{95}H_{76}O_{27}$, m. p. 113°, $[\alpha]_D^{20.5}$ +106·8°, *hendeca-*p*-chlorobenzoate*, $C_{95}H_{65}O_{27}Cl_{11}$, m. p. 130—132°, *hendeca-*p*-bromobenzoate*, $C_{95}H_{65}O_{27}Br_{11}$, m. p. 136—138°, $[\alpha]_D^{20.5}$ +85·2°, *hendecapalmitate*, $C_{194}H_{362}O_{27}$, m. p. 53°, $[\alpha]_D^{20.5}$ +31·8°, *hendecastearate*, $C_{216}H_{406}O_{27}$, m. p. 62°, $[\alpha]_D^{20}$ +28·3°, *hendecacerotate*, $C_{304}H_{582}O_{27}$, m. p. 68°, *hendecahexabromostearate*, $C_{216}H_{340}O_{27}Br_{66}$, m. p. 147—148°, $[\alpha]_D$ ca. +12°, and *hendecanaphthalenesulphonate*, $C_{128}H_{98}O_{38}S_{11}$, m. p. ca. 126°.

Sucrose:—octacinnamate, $C_{84}H_{70}O_{19}$, m. p. 87—88°, $[\alpha]_D^{18}$ +12·5°, and *octa-*p*-bromobenzoate*, $C_{68}H_{46}O_{19}Br_8$, m. p. 116—118°, $[\alpha]_D$ +27°.

*Dulcitol:—hexa-*p*-chlorobenzoate*, $C_{48}H_{32}O_{12}Cl_6$, m. p. 238°, and *hexapalmitate*, $C_{102}H_{194}O_{12}$, m. p. 74°, both optically inactive.

d-*Mannitol:—hexa-*p*-bromobenzoate*, $C_{48}H_{32}O_{12}Br_6$, prisms, m. p. 96°, $[\alpha]_D^{18}$ +29·6°.

*Inositol:—hexa-*p*-bromobenzoate*, $C_{48}H_{30}O_{12}Br_6$, prisms, m. p. 264°, optically inactive.

All optical data refer to solutions in chloroform. J. K.

Diastereomeric Acyl Derivatives of some Sugars. SVEN ODÉN (*Arkiv Kem. Min. Geol.*, 1918—1919, **7**, No. 16, 1—16).—The acylation of *d*-glucose by treatment with acid chlorides and quinoline required some days for completion at temperatures of 30—70°. In all cases, the product, corresponding in its sparing solubility in alcohol with those obtained in other instances (see preceding abstracts), was accompanied by an isomeride, easily soluble in alcohol, and differing in m. p. and specific rotation. The less soluble modifications were also obtained as sole products by the acylation of β-*d*-glucose, usually at rather higher temperatures, and are therefore to be derived from β-*d*-glucose, whilst the more soluble forms correspond with α-*d*-glucose. Similar results were obtained with *d*-galactose and *l*-arabinose. In these cases, the author designates the parent sugar, of which only one solid form is known, and that modification of the acylated sugar which is analogous in respect of melting point, specific rotation, and solubility. The following compounds are described: *penta-anisoyl-*d*-glucose*, $C_{40}H_{42}O_{16}$, α-form m. p. 98°, $[\alpha]_D^{19.5}$ +103°, and the β-form, amorphous, m. p. 175° $[\alpha]_D^{20}$ +11°; *penta-*p*-nitrobenzoyl-*d*-glucose*, $C_{41}H_{27}O_{21}N_5$, α-form m. p. 235° (decomp.), $[\alpha]_D^{19}$ +176°, soluble in chloroform, and the β-form, m. p. ca. 265° (decomp.), insoluble in chloroform; *penta-*p*-bromobenzoyl-*d*-glucose*, $C_{41}H_{27}O_{11}Br_5$, α-form, crystals, m. p. 197°, $[\alpha]_D$ +110°, and the β-form, amorphous, m. p. 220°, $[\alpha]_D$ +83°; *penta-*p*-bromobenzoyl-*d*-galactose*, $C_{41}H_{27}O_{11}Br_5$, α-form needles, m. p. 130°, $[\alpha]_D$ +45°, and the β-form, prisms, m. p. 207·5°, $[\alpha]_D$ +107°; *tetra-*p*-bromobenzoyl-*l*-arabinose*,

$C_{33}H_{22}O_9Br_4$,

α-form, m. p. 205°, $[\alpha]_D^{20}$ +383°, and the β-form, m. p. 118°, $[\alpha]_D$ +228°; *hexa-*p*-nitrobenzoyldulcitol*, $C_{48}H_{32}O_{24}N_6$, crystals, m. p. 265—268°; *octa-*p*-nitrobenzoylsucrose*, $C_{68}H_{46}O_{35}N_8$, amorphous m. p. 150° (decomp.); *tetra-*p*-nitrobenzoyl-*2:4:6*-tribromophenol* d-*glucoside*, $C_{40}H_{25}O_{13}N_4Br_3$, amorphous, m. p. 247°, $[\alpha]_D$ −39°

and *tetrapalmityl*-l-*arabinose*, $C_{69}H_{134}O_9$, amorphous, m. p. 69·5°, $[\alpha]_D^{19}$ +4°.

All optical data refer to solutions in chloroform. J. K.

The Theory of Colour Lakes. C. BRENNER (*Helv. Chim. Acta* 1920, **3**, 90—103).—See this vol., ii, 194.

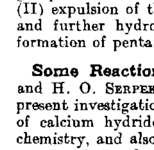
Catalytic Reduction of Furfuraldehyde. HANS PRINGSHEIM and HARTMUT NOTH (*Ber.*, 1920, **53**, [*B*], 114—118).—The hydrogenation of furfuraldehyde has already been studied by Padoa and Ponti (A., 1907, i, 146), and that of furan by Bourguignon (A. 1908, i, 280). A new study of this subject has now supplied a connecting link between the earlier results. By arranging that the furfuraldehyde is exposed to the reduced nickel as much as possible the authors have obtained furan, 1-methylfuran, and a dihydrofuran, besides the products described by Padoa and Ponti. It appears, therefore, that the hydrogenation of furfuraldehyde proceeds in three ways concurrently: (I) reduction of the aldehyde group as far as methyl, and then hydrogenation of the ring (II) expulsion of the aldehyde group with the formation of furan and further hydrogenation; and (III) rupture of the ring and formation of pentan-β-ol and methyl propyl ketone. J. C. W.

Some Reactions of Calcium Hydride. SIGISMOND REICH and H. O. SERPEK (*Helv. Chim. Acta*, 1920, **3**, 138—144).—The present investigation was undertaken on account of the importance of calcium hydride as a reducing agent, particularly in organic chemistry, and also because the data recorded by Moissan, by Erdmann and van der Smissen (A., 1908, ii, 587), and by Mayer and Altmayer (A., 1908, i, 845) are discordant in many respects.

Carbon monoxide is reduced by calcium hydride heated to dull redness, with the formation of hydrogen, methane, and formaldehyde, rather more than 16% of the carbon monoxide being converted into the latter. When a mixture of the hydride with sodium hydrogen carbonate is gently heated, formic acid is produced, the yield being 13·2% of that theoretically possible; a similar result is obtained when normal sodium carbonate is used. Ammonia is formed in small amount when nitrogen is passed over calcium hydride at about 500°, but the main reaction appears to consist in the formation of calcium nitride,

$$3CaH_2 + N_2 = Ca_3N_2 + 3H_2.$$

Acetone reacts energetically with finely divided calcium hydride. giving mesityl oxide, b. p. 128—130°, and the *substance* (annexed formula), b. p. 226—236°; acetophenone also yields condensation products with calcium hydride at 240°, but these have not been fully investigated.



Quinoline is converted at 220° into ββ-diquinolyl, needles, m. p. 190°, whilst pyridine at 160—165° yields a small quantity of crystalline matter,

m. p. 54—56°, which does not appear to be identical with any known dipyridyl.

Other organic compounds, such as ethyl acetate, benzene, nitrobenzene, and anthraquinone, did not appear to react with calcium hydride under varying conditions of temperature. Calcium hydride, therefore, only appears to react as a reducing agent at very high temperatures, and its use in the hydrogenation of organic compounds must be very limited, the more so since its action, when it does occur, appears to lead preferably to condensations.

When calcium hydride is added to an ethereal solution of ferric chloride, hydrogen is evolved, and a brown precipitate is produced which is soluble in water to an acid solution; its composition is represented by the formula $Ca_3FeCl_5(C_4H_{10}O)_8$. H. W.

Dipicrates of Arginine and Histidine. L. HUGOUNENQ and G. FLORENCE (*Bull. Soc. Chem. Biol.*, 1919, **1**, 102—106).—The dipicrates have been prepared by the action of picric acid on the monopicrates in ethereal solution. *Arginine dipicrate*,

$C_6H_{14}O_2N_4,(C_6H_3O_7N_3)_2$,

m. p. 156° (corr.), forms spherules of fine needles, and *histidine dipicrate*, $C_6H_9O_2N_3,(C_6H_3O_7N_3)_2,5H_2O$, long needles, m. p. 80°.

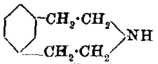
J. C. D.

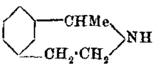
Synthesis of some Purine Glucosides. BURCKHARDT HELFERICH and MALTE VON KÜHLEWEIN (*Ber.*, 1920, **53**, [*B*], 17—22. Compare Fischer and Helferich, A., 1914, i, 333).—By the interaction of the silver salts of purines with acetobromogalactose and acetobromoarabinose, followed by hydrolysis of the acetates with methyl-alcoholic ammonia, further purine-glucosides have been obtained, as follows. *Tetra-acetyltheophylline*-d-*galactoside*, $C_7H_7O_2N_4{\cdot}C_6H_7O_5Ac_4$, has m. p. 135—137° (corr.), $[\alpha]_D^{20}$ $-13{\cdot}97°$, 12·96°, in toluene, and *theophylline*-d-*galactoside* forms long needles, m. p. 251° (corr.; decomp.), $[\alpha]_D^{20}$ $+23{\cdot}45°$, in water. *Tetra-acetyltheobromine*-d-*galactoside* crystallises in microscopic needles, m. p. 208° (decomp.), $[\alpha]_D^{17}$ $+9{\cdot}76°$, in chloroform, and *theobromine*-d-*galactoside* forms minute needles with $2H_2O$, decomp. above 150°, and is very speedily decomposed by water. *Triacetyltheophylline*-l-*arabinoside* forms thin, rhombic plates, m. p. 214—216°, $[\alpha]_D^{22}$ $+43{\cdot}34°$, in *s*-tetrachloroethane, and *theophylline*-l-*arabinoside* crystallises in slender needles, m. p. 276—277°, $[\alpha]_D^{16}$ $+34{\cdot}08°$, in water. J. C. W.

The Condensation of Ethyl Acetoacetate with *p*-Dimethylaminobenzaldehyde and Ammonia. LEONARD ERIC HINKEL and HERBERT WILLIAM CREMER (T., 1920, **117**, 137—140).

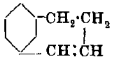
Influence of Hydrogen-ion Concentration on the Volatility of Indole from Aqueous Solution. HARPER F. ZOLLER (*J. Biol. Chem.*, 1920, **41**, 37—44).—The range of most rapid volatilisation of indole from the aqueous solutions studied is from p_H 8·0 to 10·5. This has led to the adoption of direct distillation in the separation of indole (this vol., ii, 203). J. C. D.

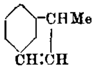
Ring Closure in the Meta-position in the Benzene Series. II. Reduction of *m*-Xylylene Dicyanide. JULIUS VON BRAUN, (FRL.) L. KARPF, and W. VON GARN (*Ber.*, 1920, **53**, [*B*], 98—109. Compare this vol., i, 87).—When *m*-xylylene dicyanide is reduced by means of sodium in alcohol, the normal product, the primary diamine, forms only about one-seventh of the yield. The chief product is a saturated, secondary amine of the formula (I) or (II).


(I.)


(II.)

It yields *iso*phthalic acid on oxidation, and the quaternary ammonium hydroxide obtained from it after treatment with methyl iodide loses, not only water, but also dimethylamine on distillation, giving an unsaturated hydrocarbon, (III) or (IV). This may


(III.)


(IV.)

be reduced to a saturated hydrocarbon, and both compounds yield *iso*phthalic acid on oxidation. This result indicates, therefore, that, contrary to all experience, the two meta-carbon atoms in the benzene ring may be connected, not only by a chain containing nitrogen, but by a simple carbon chain also.

m-*Di-β-aminoethylbenzene*, $C_6H_4(CH_2\cdot CH_2\cdot NH_2)_2$, is a colourless liquid with b. p. 165—170°/20 mm. It absorbs carbon dioxide from the air, forms a *dihydrochloride*, m. p. 290°, a *platinichloride*, m. p. 238°, and a *picrate*, m. p. 238°. Unlike the corresponding diamine of the ortho-series (A., 1917, i, 130), it reacts with methyl iodide to form a *bisquaternary iodide*, $C_6H_4(CH_2\cdot CH_2\cdot NMe_3I)_2$, m. p. 212°.

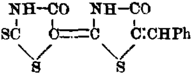
The secondary *amine*, (I) or (II), has b. p. 97—98°/16 mm., and forms a *hydrochloride*, m. p. 160°, a *platinichloride*, m. p. 232°, a sulphur-yellow *picrate*, m. p. 176°, a *benzoyl* derivative, leaflets, m. p. 72°, a *phenylthiocarbamide*, $C_{10}H_{12}N\cdot CS\cdot NHPh$, leaflets, m. p. 87°, an oily *nitroso*-compound, and a *quaternary methiodide*, $C_{10}H_{12}NMe_2I$, leaflets, m. p. 236° (corresponding *chloride*, and *platinichloride*, $C_{24}H_{36}N_2Cl_6Pt$, m. p. 228°). It also reacts with *o*-xylylene dibromide to form the *compound*, $C_{10}H_{12}\underset{\text{Br}}{\text{N}}{<}{}^{CH_2}_{CH_2}{>}C_6H_4$, m. p. 168—169°. The unsaturated *hydrocarbon*, (III) or (IV), is a mobile liquid with intense, characteristic odour, b. p. 62—63°/18 mm., D_4^{19} 0·900 (unusually low compared with the isomeric hydrocarbons, $C_{10}H_{10}$), n_D^{19} 1·54029. It polymerises like styrene, and forms a *dibromide*, m. p. 48°. On reduction by means of colloidal

palladium, it yields the *hydrocarbon*, $C_{10}H_{12}$, which is a mobile liquid with pleasant odour and abnormally low density, b. p. 50·5—51·5°/14 mm., $D_4^{17·3}$ 0·852, $n_D^{17·3}$ 1·4968. J. C. W.

Preparation of 3 : 6-Diaminoacridine. POULENC FRÈRES and ROBERT MEYER (Brit. Pat. 137214).—*m*-Phenylenediamine is melted at 130° with formic acid, or oxalic acid and glycerol, or other polyhydric alcohol, and a condensing agent such as anhydrous zinc or calcium chloride; when the evolution of carbon dioxide has ceased, the temperature is raised to, and maintained for two hours at, 150—170°, and the diaminoacridine is isolated from the resultant, almost solid mass by treatment with water and ammonia. It may be purified through its sulphate, which is sparingly soluble in very dilute sulphuric acid. [See, further, *J. Soc. Chem. Ind.*, 1920, March.] G. F. M.

Rhodanines. CH. GRÄNACHER (*Helv. Chim. Acta*, 1920, **3**, 152—163).—The author has attempted to elucidate the constitution of Nencki's rhodanine red, but great difficulty has been experienced in purifying the dye, since it could not be caused to crystallise; analyses of the product, moreover, show it to be more complex than was anticipated. It has, however, been shown that the imino-hydrogen of the rhodanine is not concerned with its oxidation by ferric chloride, since *N*-substituted rhodanines, such as 3-phenylrhodanine, also yield red dyes under suitable conditions. On the other hand, benzylidenerhodanine is not affected by ferric chloride, so that the presence of a free methylene group appears essential to the production of a dye.

Rhodanine appears to be tautomeric with 4-hydroxy-2-thiolthiazole, since it can be readily transformed in alkaline solution into the colourless benzoyl derivative, $S<\begin{matrix}C(SBz)N\\CH{=\!=}C{\cdot}OBz\end{matrix}$, whilst if the methylene hydrogen atoms are substituted, as in benzylidenerhodanine, the yellow monobenzoyl derivative, $S<\begin{matrix}C(SBz){=\!=}N\\C(:CHPh){\cdot}CO\end{matrix}$ is produced. Alkylidenerhodanines react with aniline and phenylhydrazine to yield the corresponding phenylhydrazones and anilides, the sulphur of the thio-keto-group being removed as hydrogen sulphide. Since aniline is comparatively readily removed from these anilides, they can be employed for condensing the rhodanine molecule with compounds containing a reactive methylene group; in this manner, benzylidenerhodanineanilide can be condensed with a second molecule of rhodanine to yield 5-benzylidene-5′-rhodanylidene-2-rhodanine (annexed formula). Reaction with aniline or phenylhydrazine proceeds in a totally different manner with rhodanines, such



as *N*-phenylrhodanine, which contain the free methylene group; in

this case, the sulphur of the thio-keto-group remains unaffected, and complete fission of the rhodanine ring occurs, with formation of thiocarbamides or thiosemicarbazides, reaction occurring so readily that the process is conveniently used for the preparation of the latter class of substances.

The following individual substances are described: *dibenzoylrhodanine*, colourless needles, m. p. 126°; 5-*benzylidene-2-benzoylmercaptothiazoline*, deep yellow leaflets, m. p. 151—152°; 5-*benzylidenerhodanine-2-phenylhydrazone*, orange-red leaflets, m. p. 219° after softening at 210°; 5-p-*dimethylaminobenzylidenerhodanine-2-phenylhydrazone*, red leaflets, m. p. 282° (decomp.); 5-*benzylidenerhodanine-2-anilide*, pink leaflets, m. p. 252—253° after softening at 248°; 5-p-*dimethylaminobenzylidenerhodanine-2-anilide*, dark yellow leaflets, m. p. 308° (hydrolysis of the two substances last named leads to the formation of 2:4-diketo-5-benzylidenethiazolidine, $\begin{matrix}\mathrm{CO—S}\\ \mathrm{NH\cdot CO}\end{matrix}\!>\!\mathrm{C{:}CHPh}$, m. p. 238—240°, and of 2:4-*diketo-5-p-dimethylaminobenzylidenethiazolidine*, long, orange-yellow needles, m. p. 296°, respectively); 5-*benzylidene-5'-rhodanylidene-2-rhodanine*, brown leaflets; *diphenylthiocarbamide*, colourless leaflets, m. p. 151—152°; *diphenylthiosemicarbazide*, long, colourless needles, m. p. 176—177°. H. W.

Acyl Substituted *iso***Thiohydantoins.** AUGUSTUS EDWARD DIXON and RAYMOND THOMAS JOACHIM KENNEDY (T., 1920, **117**, 74—79).

p-**Cymylene-2 : 6-diamine and the Formation of 2 : 4-Dinitrotoluene by the Nitration of** *p*-**Cymene.** J. ALFTHAN (*Ber.*, 1920, **53**, [*B*], 78—98).—With a view to the utilisation of the large quantities of *p*-cymene which accumulate in the sulphite-cellulose industry (1 kilo. per ton of cellulose), Aschan has studied the nitration of the hydrocarbon (*Finska Kemistsamfundets Meddelanden*, 1916, **25**, 122). The conditions finally adopted, and now described, are the gradual addition of one part of cymene to a mixture of two parts of nitric acid (D 1·5) and four parts of sulphuric acid (1·84), the temperature being kept below 0°. The main product is a crude dinitro-derivative, which may be reduced to a crude diamine. When this is examined, it is found to consist of some 2:4-tolylenediamine, but chiefly *p*-cymylene-2:6-diamine, a new base. The occurrence of the toluene derivative therefore suggests that 2:4-dinitrotoluene is present in the nitration product, the *iso*propyl group having been expelled by a nitro-group. The mechanism of this displacement is discussed, but various probable suggestions are negatived by experience, and the question is left open. There also seems to be little hope of making the dinitrotoluene the main product, and so utilising cymene as a source of trinitrotoluene.

The separation of the products of nitration is a difficult matter,

distillation under reduced pressure being the best method. The crude product is partly oily and partly solid, the latter yielding 2:4-dinitrotoluene, m. p. 70°, b. p. below 161°/6 mm., and 2:6-dinitro-*p*-cymene, m. p. 54°, b. p. 161—163°/6 mm. The oil contains, in addition, cymene, *p*-tolyl methyl ketone, and a mononitrocymene, which can be converted into the above dinitrocymene. The crude dinitro-compounds are reduced by means of tin and zinc and hydrochloric acid (tin at the commencement, zinc after the reaction has set in), and the crude diamines separated by fractional distillation under 15 mm. pressure.

2:4-Tolylenediamine, purified by crystallisation from benzene, forms pale yellow, very hard needles, m. p. 98—99°, b. p. 160—168°/15 mm., and p-*cymylene*-2:6-*diamine*,

$$[Me:Pr^{\beta}:NH_2:NH_2=1:4:2:6],$$

separates from 20% alcohol in glistening, thin leaflets, m. p. 95—96°, b. p. 300—300·5°/768 mm., 158—162°/10 mm., 0·7469 gram dissolving in 100 grams of water at 25°. The following salts of *p*-cymylene-2:6-diamine are described: *hydrochloride*, needles, decomp. 180—200°; characteristic *zincichloride*,

$$C_{10}H_{12}(NH_2,HCl)_2,ZnCl_2,$$

pale pink needles, decomp. above 245°; *hydrogen sulphate*,

$$B,2H_2SO_4,$$

decomp. 250°; *nitrate*, long leaflets, decomp. 170°; *hydrogen oxalate*, $B,2H_2C_2O_4$, rods, m. p. 188—189° (decomp.); and *thiocyanate*, needles, m. p. 137°. The *diacetyl* derivative,

$$C_{10}H_{12}(NHAc)_2,$$

crystallises in thin needles, m. p. 254°, and yields a 3-*nitro*-compound, needles, m. p. 280—282°, which may be hydrolysed to 3-*nitro*-p-*cymylene*-2:6-*diamine*, yellow needles, m. p. 187°. The *dibenzoyl* derivative forms needles, m. p. 246—247°.

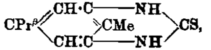
Condensation products of the cymylenediamine are as follows: with formaldehyde, 2:6-*bismethyleneimino*-p-*cymene*,

$$C_{10}H_{12}(N:CH_2)_2,$$

m. p. 170—180° (decomp.); from the chloride and potassium cyanate or thiocyanate, 2:6-*dicarbamido*-p-*cymene*,

$$C_{10}H_{12}(NH\cdot CO\cdot NH_2)_2,$$

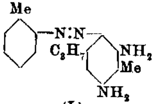
needles, m. p. 270—280° (decomp.), and 2:6-*dithiocarbamido*-p-*cymene*, m. p. 165—175° (decomp.); with carbon disulphide and alcoholic potassium hydroxide, 2-*methyl*-5-iso*propyl*-1:3-*phenylenethiocarbamide*,



m. p. 157—158°; and with alcoholic oxalic acid, m-*aminocymyloxamic acid*, $NH_2\cdot C_{10}H_{12}\cdot NH\cdot CO\cdot CO_2H$, m. p. 217—218° (decomp.).

The following dyes have also been prepared: a dark red *hydroxyazo*-dye, $C_{30}H_{22}O_{14}N_4S_4Na_4$, by diazotising at a low temperature, to avoid the production of a Bismarck-brown, and coupling with sodium β-naphthol-3:6-disulphonate; a *chrysoidine* of the

formula (I), reddish-yellow cubes, m. p. 114—115°, by coupling with diazotised *o*-toluidine; and a brownish-yellow *eurhodine*, m. p.



(I.)

(II.)

177—178°, of the formula (II), by condensation with *p*-nitrosodimethylaniline. J. C. W.

2-Nitro-4-cyanobenzaldehyde and 6 : 6′-Dicyanoindigotin. S. Reich and E. Lenz (*Helv. Chim. Acta*, 1920, **3**, 144—151).—2-*Nitro-p-toluonitrile*, colourless, shining needles, m. p. 107°, is prepared from 2-nitro-*p*-toluidine by a modification of the method of Niementowski and Noyes, and is converted by *p*-nitrosodimethylaniline in alcoholic solution in the presence of sodium carbonate into p-*dimethylaminophenyl-2-nitro-4-cyanophenylazomethine* [2-*nitro-4-cyanobenzylidene*-p-*phenylenedimethyldiamine*],

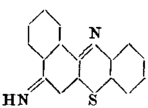
$$NMe_2\cdot C_6H_4\cdot N:CH\cdot C_6H_3(CN)(NO_2),$$

almost black needles, m. p. 182·5—183° (decomp.), which is hydrolysed by hydrochloric acid, yielding 2-*nitro-4-cyanobenzaldehyde*, red needles, m. p. 110°. The latter yields an *oxime*, red needles, m. p. 142—143°, and a *phenylhydrazone*, bright red crystals, m. p. 202—203° (decomp.), which could not be converted by potassium hydroxide in aqueous-alcoholic solution into an *iso*indazole derivative, a fact which is interpreted as further evidence in favour of Reich's views on the influence of the accumulation of atoms and atomic groups round the aldehydic carbon atom on such condensations (compare Reich and Nicolaeva, A., 1919, i, 171). The aldehyde, when dissolved in benzene, is converted by exposure to sunlight into 2-*nitroso-4-cyanobenzoic acid*, small, yellow crystals, which begin to darken at about 210°, and have m. p. 250° (decomp.). When a solution of the aldehyde in acetone is treated with dilute sodium hydroxide solution, 6:6′-*dicyanoindigotin* is deposited as a bluish-violet powder with metallic lustre; when heated, it does not sublime, but decomposes, with evolution of reddish-violet vapours. When reduced with sodium hyposulphite, it dyes wool and cotton from an alkaline bath in reddish-purple shades, which become blue with a tinge of violet on exposure to air, oxidation proceeding more slowly than with indigotin. The shades are fast to light and milling. H. W.

Preparation of Easily Soluble Compounds of the *CC*-Dialkyl-, *CC*-Diallyl-, and *CC*-Alkylaryl-barbituric Acids. F. Hoffmann, La Roche & Co. (Brit. Pat. 122778).—Easily soluble compounds of these acids are obtained by combining them with alkylamines, for example, diethylamine or dimethylamine, by add-

ing rather more than the theoretical amount of alkylamine to the free acid, so that the latter is dissolved, and then evaporating off the excess of amine. The products are more powerful hypnotics than the free acids, and much more stable in aqueous solution than their sodium salts.

Action of *o*-Aminothiophenol on Orthoquinones. I. 5-Imino-7 : 12-naphthaphenthiazine. KNUT STAHRFOSS (*Helv. Chim. Acta*, 1920, **3**, 134—138).—*o*-Aminothiophenol hydrochloride reacts with 4-amino-1 : 2-naphthaquinone in boiling 80% acetic acid solution, with formation of 5-*imino*-7 : 12-*naphthaphenthiazine hydrochloride*, a chocolate-brown powder, which is stable in air and readily soluble in water. The *platinichloride* was analysed. The free *base* (annexed formula) is an unstable, yellow substance. The constitution of the substance follows from the conversion of the hydrochloride by concentrated sulphuric acid into a naphthaphenazthione, identical with that formed from *o*-aminothiophenol and 4-hydroxynaphthaquinone. H. W.



New Bases for the Preparation of Mordant Dyes. HEINRICH BAMBERGER (*Zeitsch. angew. Chem.*, 1920, **33**, i, 8).—The chlorides of *o*-nitrophenol-*p*-sulphonic acid, 6-nitro-*o*-cresol-*p*-sulphonic acid, and 6-nitrosalicyl-*p*-sulphonic acid, obtained by treatment of their potassium salts with chlorosulphonic acid, react quantitatively with aromatic amines, diamines, amino-carboxylic acids, or amino-phenols, and with amino-sulphonic acids or amino-phenolsulphonic acids of the benzene or naphthalene series. By reducing the resulting sulphamido-compounds with sodium sulphide, valuable bases are produced for mono- and bisazo-mordant dyes, which give colours ranging from yellow to bluish-violet (compare Swiss Pat. 81249—81256; Fr. Pat. 490177 [1918]). J. K.

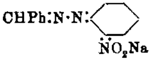
Certain Salts with para-, ortho-, and meta-Quinonoid Structure. R. CIUSA (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 366—371).—In contact with alkali, best in acetone solution, *p*-nitrophenylhydrazones are turned violet, addition of water to the solution or acidification yielding the initial hydrazones unchanged. That the corresponding salts, which are easily obtainable, differ in structure from the nitrohydrazones themselves is shown by their different colour in solution and by their different absorption spectrum. To explain the intense colour of these salts, the simple quinonoid constitution is insufficient, the assumption of the more complex formula, $C_6H_4<^{NO_2M\cdots\cdots}_{N[\cdot N:CHPh]\cdots}$, in which the metal, M, is united by secondary valencies to the rest of the molecule, being necessary; the position at which the secondary valencies act is still uncertain. Similar complex formulæ are attributed to all the

quinonoid salts dealt with in the paper. The following salts have been prepared: the potassium salt of benzaldehyde-*p*-nitrophenylhydrazone, CHPh:N·N:C_6H_4:NO_2K; the disodium salt of benzylidenepyruvic acid-*p*-nitrophenylhydrazone,

$$CHPh:CH\cdot C(CO_2Na):N\cdot N:C_6H_4:NO_2Na;$$

the dipotassium salt of benzoylglyoxylic acid-p-nitrophenylhydrazone, CO_2K·CBz:N·N:C_6H_4:NO_2K.

In alcoholic or acetone solution, *o*-nitrophenylhydrazones also *dissolve in alkali, the solutions assuming a blue coloration.* Crystalline salts of benzaldehyde-*o*-nitrophenylhydrazone have not been obtained, although the sodium salt (I) certainly exists in solution,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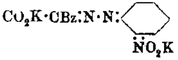

(II.)

but the dipotassium salt of benzoylglyoxylic acid-*o*-nitrophenylhydrazone (II) has been prepared in shining, bronze-coloured crystals or as a blue powder.

It has been stated that benzophenone-*m*-nitrophenylhydrazone does not undergo salt formation in contact with alcoholic potassium hydroxide. The author finds, however, that a very slight change of colour does take place under these conditions, and that, in acetone solution, *m*-nitrophenylhydrazones give a green coloration with the alcoholic alkali, addition of water then resulting in the formation of the unaltered nitrophenylhydrazones. The *absorption spectrum of such an alkaline solution differs from that of the* original hydrazone, and persists even on dilution of the liquid. In this case, it has not been found possible to obtain crystallised salts, *but it may be assumed that the salt formation occurs with change* from the benzenoid to the *m*-quinonoid structure,

$$CHPh:N\cdot N:C_6H_4:NO_2M;$$

such m-quinonoid saline compounds are certainly readily hydrolysable, and the tendency to their formation small.

The experimental results are to be published elsewhere.

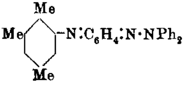
T. H. P.

Amine-oxidation. II. Bivalent Nitrogen. Triphenylhydrazyl. STEFAN GOLDSCHMIDT (*Ber.*, 1920, **53**, [*B*], 44—62).—When an ethereal solution of triphenylhydrazine (Wieland, A., 1915, i, 797) is shaken with lead peroxide, a fugitive, deep blue solution is formed which has the characteristics of solutions of compounds with bivalent nitrogen (Wieland, *ibid.*, 848). This suggests that oxidation to *hexaphenyltetrazane* has taken place, this being dissociated in solution into *triphenylhydrazyl*, thus: $2NPh_2\cdot NHPh \longrightarrow NPh_2\cdot NPh\cdot NPh\cdot NPh_2 \longrightarrow 2NPh_2\cdot NPh\cdots\cdots$ By carrying out the oxidation in methyl ether at $-55°$ to $-60°$, the tetrazan may actually be isolated as a very pale green crust, which is sparingly soluble in chilled ether or light petroleum, but more soluble in toluene or chloroform. The solutions are deep blue and

do not obey Beer's dilution law, thus confirming the idea of dissociation. The dissociation depends on temperature and on the solvent. For example, ethereal solutions, which are only pale greenish-blue at $-80°$, are deep blue at the ordiuary temperature, aud chloroform solutions are darker than ethereal solutions under the same conditions. The substance may be analysed by means of quinol, this causing reduction to triphenylhydrazine, when the liberated quinone can be titrated iodometrically.

Triphenylhydrazyl is not sensitive to oxygen, but combines with nitric oxide at low temperatnres to form *N*-nitrosotriphenylhydrazine, golden prisms, m. p. 115° (Busch, A., 1907, i, 552). It also combines with triphenylmethyl, but this agent reacts too slowly to permit of the isolation of a pure product before the triphenylhydrazyl has decomposed. The decomposition of triphenylhydrazyl is accompanied by change of colour, through green to reddish-brown, the products being diphenylamine and quinoneanildiphenylhydrazone, $NPh_2{\cdot}N{:}C_6H_4{:}NPh$ (Wieland, A., 1911, i, 82). Ethereal solutions of triphenylhydrazine also develop the blue colour of triphenylhydrazyl on exposure to sunlight, and then yield the same decomposition products.

When a mixture of aniline and triphenylhydrazine in ether is oxidised by lead peroxide, benzoquinoneanildiphenylhydrazone is again formed. This is interpreted as the fusion of the two radicles, $NPh_2{\cdot}NPh{\cdot} + {:}NPh \longrightarrow NPh_2{\cdot}N{:}C_6H_4{:}NPh$ (compare this vol., i, 226), and is confirmed by the fact that a mixture of cumidine and triphenylhydrazine gives a homologous *compound* (annexed formula), which crystallises in the form of its *hydrochloride* in bluish-violet, stout spikes, m. p. 152—153°. Both compounds exhibit only one absorption band, the aniline derivative at 465—650 $\mu\mu$ and the new one at 475—525 $\mu\mu$. The identity of the new compound is established by reduction to diphenylamine and p-*aminophenylcumylamine*, $NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_2Me_3$, concentric groups of needles, m. p. 86—87°.



These facts are discussed in connexion with Wieland's views on the decomposition of triphenylhydrazine. It is suggested that the products are best interpreted by assuming an initial dissociation into H and $NPh_2{\cdot}NPh{\cdot}$.

When triphenylhydrazine is treated with ethereal hydrogen chloride at $-20°$, it yields *N*-phenylbenzidine (Busch, *loc. cit.*). This is oxidised by lead peroxide in ether to *diphenoquinonephenyldi-imine*, $NPh{:}C_6H_4{\cdot}C_6H_4{:}NH$, yellowish-red needles, m. p. 180—181°. J. C. W.

Hæmoglobin. I. Optical Constants. WILLIAM H. WELKER and CHARLES SPENCER WILLIAMSON (*J. Biol. Chem.*, 1920, **41**, 75—79).—By employing the method of Marshall and Welker (A., 1913, ii, 568) for removing small amounts of other colloids from

hæmoglobin solutions, the authors were able to prepare purer specimens of crystallised hæmoglobin, which could be used for the study of the absorption coefficients of the pigment from various species. The results obtained indicate that there is not sufficient *difference* in the absorption coefficients of the hæmoglobin of various species *to serve as a means of identification* of the species. J. C. D.

The Structure of Yeast-nucleic Acid. V. Ammonia Hydrolysis. P. A. Levene (*J. Biol. Chem.*, 1920, **41**, 19—23).—The fourth nucleotide, *cytidinephosphoric acid*, $C_9H_{14}O_8N_3P$, m. p. 225° (corr.; decomp.), $[\alpha]_D^{20}$ +40—43°, has now been obtained in a crystalline condition. There is a danger of error in assuming the existence of di- or tri-nucleotides on the basis of the results of elementary analysis, for it is shown that the free nucleotides, as well as their brucine salts, are capable of forming mixed crystals, which may furnish analytical data very nearly approaching those required by polynucleotides. J. C. D.

Crystalline Uridinephosphoric Acid. P. A. Levene (*J. Biol. Chem.*, 1920, **41**, 1—2).—The crystalline diammonium salt of uridinephosphoric acid was converted into the lead salt, which was decomposed by hydrogen sulphide. From the concentrated filtrate, the free uridinephosphoric acid, $C_9H_{13}O_9N_2P$, was obtained in a crystalline condition, m. p. 202° (corr.; decomp.), $[\alpha]_D^{20}$ +10·5°. This research marks an important step in the chemistry of yeast-nucleic acid, as every one of the four constituent nucleotides has now been prepared in crystalline form. J. C. D.

Physiological Chemistry.

Estimation of the Alkalinity of Blood. Pedro J. Pando (*Rev. Farm., Buenos-Ayres*, 1919, 167; from *J. Pharm. Chim.*, 1919, [vii], **20**, 394—395).—A small flask containing 20 c.c. of water, 1 gram of 10% sodium citrate solution, and 10 c.c. of *N*/200-sulphuric acid is weighed; about 0·2 gram of blood is collected directly in the flask, which is again weighed. After the addition of 1 gram of animal charcoal, the mixture is diluted to 50 c.c., filtered, and 45 c.c. of the filtrate are titrated with *N*/200-sodium hydroxide solution, using phenolphthalein as indicator. By this method, normal blood exhibits an alkalinity equivalent to 5·50 grams of sodium hydroxide per 1000 grams. W. P. S.

The Presence of Hæmatin in Human Blood Serum. III. Further Results from Toxicological Practice. Joh. Feigl (*Biochem. Zeitsch.*, 1919, **93**, 119—127. Compare A., 1918, i, 241).—From observations made on munition workers, it was found that

hæmatinæmia is an important phenomenon in the course of th decomposition of blood brought about by the toxic effect of nitrou fumes (NO_2,N_2O_3), and is more apparent than the contemporar incipient methæmoglobinæmia. Out of about thirty cases of ga poisoning (from the front), eight showed hæmatinæmia ten t twenty-eight days after the intoxication. No definite informatio as to the presence of hæmatin in the serum of "Röntgen gas" cases is so far available. Hæmatinæmia was absent in cases o zinc, copper, and lead poisoning. A case of arsenic hydride poison ing showed hæmatinæmia. The histories of some of the cases ar given. S. S. Z.

Antigens. XIII. The Significance of the Protein Components in the Precipitin Reaction of the Azoproteins. KARL LANDSTEINER (*Biochem. Zeitsch.*, 1919, **93**, 106—119. Compare A., 1918, i, 321).—Immune sera were prepared by the injection of azotised horse sera, prepared by the coupling of the serum with the diazo-compounds of aniline-*m*-sulphonic acid and *p*-arsanilic acid respectively. The precipitin reactions of the sera were then tested on various proteins azotised by means of the diazo-compounds of aniline-*m*-sulphonic acid and *p*-arsanilic acid. With the exception of gelatin and peptone, the aniline-*m*-sulphonic acid immune serum precipitated all the proteins azotised by means of the aniline-*m*-sulphonic diazo-derivative, but not the proteins azotised with the *p*-arsanilic acid derivative. The reverse happened with *p*-arsanilic acid immune serum. The author suggests that the usual immunological serum reactions do not depend on the specific chemical structure of the respective proteins, but on the dimensions of the molecule of these proteins. S. S. Z.

Availability of Carbohydrate in certain Vegetables. W. H. OLMSTED (*J. Biol. Chem.*, 1920, **41**, 45—58).—Vegetables of low carbohydrate content, such as cabbage, spinach, and lettuce, are frequently employed in the diet of patients with diabetes. Estimations of the sugar-forming material in such vegetables were therefore made, either by hydrolysis of the starch with diastase, followed by estimation of the dextrose by reduction of copper solutions, or by ascertaining the extra sugar excreted by a phloridzinised dog after administration of a known amount of the vegetable. The amounts of available carbohydrate in cabbage and cauliflower, as measured by the latter method, are of the same order as those recorded in the analyses of Atwater and Bryant. The "thrice cooking" process frequently employed to remove carbohydrates from vegetables intended for consumption by diabetic patients is effective in reducing the amount of carbohydrate present by 90%. J. C. D.

The Influence of Alkaline and Acid Hydrolysis on the Absorption and Utilisation of Proteins. I. The Utilisation of Hydrolysed Casein. JOHANNES MÜLLER and HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1919, **93**, 34—44).—Various

hydrolysis preparations of casein were fed to a terrier, and the nitrogen metabolism was worked out in order to ascertain the amount of the protein utilised by the animal. 96·1% of the original casein was retained by the dog. The same casein, hydrolysed by shaking with 3% sodium hydroxide and heating it for one and a-quarter hours in a boiling water bath under a reflux condenser, was only utilised to the extent of 59%. When the casein was heated with 3% sodium hydroxide for two hours under a pressure of four atmospheres, 39% of the hydrolysed product was retained. The administration of opium per os to the dog fed on the alkaline product of hydrolysis of casein did not improve its retention in the organism. On the other hand, 98·6% of the casein, hydrolysed by heating it with 2·74% hydrochloric acid in a boiling water bath under a reflux condenser for four hours, was utilised. Protalbic acid, prepared by hydrolysing casein with 3% sodium hydroxide under a reflux condenser and precipitating with acetic acid, was also tried. 29% of this product was retained. S. S. Z.

The Utilisation of Yeast in the Animal Organism. W. Völtz (*Biochem. Zeitsch.*, 1919, **93**, 101—106. Compare Schill, A., 1918, i, 359).—Living yeast, after a sojourn of six and a-half hours in the digestive tract of a dog, was excreted in the fæces in a living condition, and was capable of fermenting sugar. After remaining for nine and a-half hours inside the dog, the yeast cells were mostly dead, and about half of them were digested. The fæces in this case contained 5% of living, 20% of diseased, and 75% of dead cells. 53·3% of the total organic matter and 46·6% of the protein of the consumed yeast were utilised by the organism. It is therefore advisable to kill the yeast before utilising it for feeding purposes unless it is administered with a therapeutic object.
S. S. Z.

Occurrence of Squalene in the Egg Oil of a Shark. Mitsumaru Tsujimoto (*J. Ind. Eng. Chem.*, 1920, **12**, 73).—The oil separated from the eggs of the Japanese shark, *Lepidorhinus kinbei* (Tanaka), by extraction with ether was a light brown, semi-solid substance with an iodine value of 177·6. When treated with dry hydrogen chloride, it yielded 20% of squalene hexahydrochloride. Squalene has also been found in the egg oil of the frill shark, *Chlamydoselachus anguineus* (Garman). [See, further, *J. Soc. Chem. Ind.*, 1920, 197A.] C. A. M.

Squalene: a Highly Unsaturated Hydrocarbon in Shark-liver Oil. Mitsumaru Tsujimoto (*J. Ind. Eng. Chem.*, 1920, **12**, 63—72).—Of the numerous species of Japanese sharks, those having liver oils of low sp. gr. (below 0·9) usually have the hydrocarbon, *squalene*, in the oil (A., 1918, i, 89). This constituent may be approximately estimated by distilling the oil under reduced pressure in a current of carbon dioxide or other inert gas. The amount thus estimated in the liver oils of twelve species of sharks ranged

from 7·1 to 84·8%. Squalene isolated from the liver oil of the Ai-zamé shark had D_4^{15} 0·8591 and D_4^{20} 0·8559. Exposed to the air in a thin layer, it absorbed 13·4% of oxygen in three days and 24·0% in twenty-three days, the oxygen absorption, calculated from the formula $C_{30}H_{50}O_6$, being 23·66%. The dodecabromide, $C_{30}H_{50}Br_{12}$, when reduced with glacial acetic acid and zinc dust, yielded about 35% of an orange-yellow oil with n_D^{20} 1·4950. The hexahydrochloride, when recrystallised from acetone, melted at about 125°. Its formation is the best test for the detection of as little as 1% of squalene in an oil. The hexahydrobromide forms white, lustrous crystals, turning brown at 115—118°, and melting at 125—126°, whilst the *hexahydriodide* is an unstable, white, crystalline compound, melting to a pink liquid at 108—109°. On dechlorinating the hexahydrochloride, a nearly colourless, oily liquid of D_4^{15} 0·9065 was obtained. When distilled under reduced pressure, this yielded an oily distillate with iodine value 281, which appeared to be a hydroxy-derivative of squalene with the formula $C_{30}H_{50}(OH)_2$. It boiled at 252—254° (4·5 mm.), and had D_4^{15} 0·8995 and n_D^{20} 1·4938. Squalene yielded a yellow formolite, which decomposed at about 180°, but no crystalline nitrosochloride or nitrosite. On dry distillation, it yielded a small fraction, which was a hydrocarbon with molecular weight 131. Although squalene differs slightly in physical properties from the hydrocarbon, spinacene, isolated by Chapman from the liver oils of Portuguese sharks (T., 1917, **111**, 56; 1918, **113**, 458), it seems probable, from the similarity of the derivatives, that the two hydrocarbons are identical. [See, further, *J. Soc. Chem. Ind.*, 1920, 197A.]

C. A. M.

Physiology of Glands. XXXVIII. The Influence of the Spleen on the Respiratory Metabolism. NIKOLA DANOFF (*Biochem. Zeitsch.*, 1919, **93**, 44—66).—The respiratory metabolism of rats was studied by means of Haldane's method. It was found that the respiratory metabolism of small animals is higher per unit body weight and time than that of larger animals, and that it rose as the surrounding temperature sank. Rats which had their spleen removed used up more oxygen and produced correspondingly more carbon dioxide than normal rats. These quantities rose from day to day soon after the operation. The respiratory quotient, however, remained the same before and after the opera-
ecoron. The presence of the spleen therefore reduces the respiratory
ooking bolism, and its function in this respect is consequently opposite
rom vegt of the thyroid.

S. S. Z.

ffective in

tion of Lactose in the Mammary Gland. F.
'*Biochem. Zeitsch.*, 1919, **93**, 237—253).—On digesting
The Influe of the mammary gland, dextrose was formed. This
bsorption then converted into lævulose and galactose, and eventu-
on of Hyd tose. These reactions were followed up by estimating
IURSCHHAUSER , the rotation, the formation of mucic acid by oxida-

tion with nitric acid, and the osazone formation. The degree of the dextrose formation and its transformation into the other sugars in the extract of the mammary gland are found to be influenced by the condition of the activity of the gland at the time of the animal's death. Sucrose, which was added to the extract, was also degraded by it, and the products of degradation underwent further transformation. The formation of dextrose in the extract could not be of the character of a glucoside hydrolysis, as on heating the extract with 2—10% sulphuric acid, the reduction was only increased to a small extent. This increase in reduction was shown to be due to the splitting of small quantities of lactose. The author advances the hypothesis that dextrose, which reaches the mammary gland through the blood stream, is not always utilised immediately, but is sometimes stored there as an intermediate substance, which by some still unknown fermentation process can be reconverted into dextrose. The latter, by further enzymic activity, is converted into lævulose and galactose, and eventually into lactose. S. S. Z.

The Normal Arsenic of Living Tissues and the Traces of Iodine found in the Air and in Waters. Some Necessary Corrections. A. Gautier (*Compt. rend.*, 1920, **170**, 261—262).—The author reaffirms the conclusions drawn from his previous work (compare A., 1900, ii, 152, 168, 226, 670; 1903, ii, 92) as to the occurrence of arsenic in animal tissues, but draws attention to possible errors in the estimation of arsenic, due to the presence of traces of hydrogen arsenide as an impurity in the hydrogen sulphide used.

Examination of further samples of sea-water from different sources, previously found to give water containing iodine in a soluble form, now shows the complete absence of iodine in a soluble form, although minute traces of it in an insoluble form were found. W. G.

Carbonic Acid and Carbonates in Cows' Milk. Lucius L. Van Slyke and John C. Baker (*J. Biol. Chem.*, 1919, **40**, 335—344).—Considerable care must be taken over the collection of the sample to ensure that there is no loss of carbon dioxide. The analysis is carried out by the method previously described for the estimation of carbon dioxide in blood plasma (Van Slyke, A., 1917, ii, 422), with one or two slight modifications, the chief of which is the employment of a 20% solution of lactic acid to disengage the carbon dioxide. With the decrease in the hydrogen-ion concentration there is a general tendency for the carbon dioxide content of milk to increase and for the degree of acidity, as measured by titration, to decrease. The results are higher than those recorded by other workers, the normal content of carbon dioxide in milk being about 10% by volume. The carbon dioxide of milk may be completely removed by exhaustion, provided the milk is spread out in a thin film and kept in motion. The removal of carbon dioxide results in a decrease in the hydrogen-ion concentration. When

milk is pasteurised, the carbon dioxide content is decreased, but the hydrogen-ion concentration is unchanged. When the carbon dioxide has been completely removed prior to pasteurisation, the hydrogen-ion concentration increases appreciably. It is suggested that the decrease of carbon dioxide in pasteurised milk might be made the basis of a method for distinguishing pasteurised from normal milk.

Carbon dioxide in milk is present as carbonic acid and as bicarbonate, probably of sodium, the ratio being about 1 to 2. The tension of carbon dioxide in milk is calculated to be about 50—55 mm. of mercury at 20° in the case of a $0{\cdot}01N$-solution with p_H value of 6·60. J. C. D.

The Influence of the Acidity of the Milk on the Velocity of Inactivation of the Peroxydase by Heat. A. Bouma and W. van Dam (*Biochem. Zeitsch.*, 1918, **92**, 385—397).—The influence of the hydrogen-ion concentration on the inactivation of the peroxydase in milk at 70·55° was studied. At 70°, the p_H is two and a-half to three times higher than at the ordinary temperature. The addition of so much lactic acid to the milk as was just insufficient to curdle it on pasteurisation had no effect on the velocity constant of the inactivation of the enzyme at that temperature. On the other hand, the addition of sodium hydroxide and ammonia greatly accelerated the destruction of the peroxydase. This confirms the preliminary observations previously made by Zilva. S. S. Z.

The Physiological Action of the Proteinogenic Amines. I. The Influence of Proteinogenic Amines on the Nitrogen Metabolism of Dogs from which the Thyroid has been Removed. J. Abelin (*Biochem. Zeitsch.*, 1919, **93**, 128—149).—Phenylethylamine, *p*-hydroxyphenylethylamine, and eventually *iso*amylamine were administered per os to dogs from which the thyroid had previously been removed. An increase in the metabolism and greater diuresis were observed as a result of the treatment. A decrease in body weight was also recorded. As the pharmacological action of the above amines resembles that of the protein substances from the thyroid, it is suggested that the action of the thyroid on the metabolism is not due to the protein substances themselves, but to derivatives emanating from them. S. S. Z.

Physiological Action of Aromatic Diamines. Richard Meissner (*Biochem. Zeitsch.*, 1919, **93**, 149—163).—*o*- and *m*-Phenylenediamines, in contradistinction to *p*-phenylenediamine, are tolerated by frogs in high doses. *o*-Phenylenediamine has also no toxic effect on rabbits. Cats, on the other hand, develop œdema typical of *p*-phenylenediamine intoxication on administration of the ortho-compound. *m*-Phenylenediamine produces no œdema in cats and rabbits, but the latter animal develops ascites. The methyl

derivatives of the above isomerides produce cerebral manifestations, and prove fatal even when given in small doses, but no œdema can be observed. The diethyl and monoacetyl derivatives, on the other hand, cause swellings in the head and neck. The insoluble diacetyl- and ethoxy-*p*-phenylenediamine are inactive. Triamino-benzene, -toluene, and -phenol produced methæmoglobinuria in cats, but not *œdema*. S. S. Z.

The Pharmacology of Compounds Resembling Digitalis in their Activity. MARGARETE WALTER (*Biochem. Zeitsch.*, 1918, **92**, 267—282).—The diffusibility, electrical charge, adsorption, and the reversibility of the action on the heart of compounds resembling digitalis in their activity were studied. No connexion between these properties could be established. S. S. Z.

Chemistry of Vegetable Physiology and Agriculture.

The Effect of Nitrogen-fixing Organisms and Nucleic Acid Derivatives on Plant Growth. W. B. BOTTOMLEY (*Proc. Roy. Soc.*, 1920, [*B*], **91**, 83—95).—The crude nucleic acid derivatives from bacterised peat and the growth products from *Azotobacter chroococcum* or from *Bacillus radicicola* each exert a very marked influence in increasing the growth of plants of *Lemna minor* in water culture. Not only is there an increase in the number of plants formed, but also in the weight of the plants. The crude nucleic acid derivatives, which are about as effective as the *Azotobacter* growth, are much more effective than the pure adenine-uracil dinucleotide derived from them. The joint effect of the crude nucleic acid derivatives and *Azotobacter* growth is much greater than the sum of their individual effects, being about equal to that of the water extract of an equivalent amount of bacterised peat. It is of interest to note that the crude nucleic acid derivatives, and the *Azotobacter* and *B. radicicola* growths, all give the Folin-Macullum reactions, which are stated to indicate the presence of vitamines. W. G.

The Oxidation of Vanillin to Vanillic Acid by certain Soil Bacteria. WILLIAM J. ROBBINS and E. C. LATHROP (*Soil Sci.*, 1919, **7**, 475—485).—In solution cultures containing mineral nutrients and vanillin, the latter being the only source of carbon, and inoculated with a bacterium present in certain Alabama soils, the vanillin was first oxidised to vanillic acid, which could be isolated, but was subsequently destroyed if left in the solution. Estes's reagent, acid mercuric nitrate, gives satisfactory results in the estimation of vanillin in the presence of vanillic acid (compare A., 1917,

ii, 343), but the phenol reagent of Folin and Denis (compare A., 1912, ii, 1011) is unsatisfactory under such conditions, as vanillic acid, like vanillin, gives a blue colour with this reagent, the colour produced by the acid being much deeper than that produced by an equivalent amount of the aldehyde. The authors find that vanillic acid has m. p. 210·5—211° (corr.). W. G.

Chemical Enzyme Studies. The Growth of Yeast in Alkaline Solutions. HANS VON EULER and OLOF SVANBERG (*Arkiv Kem. Min. Geol.*, 1918, 7, No. 11, 1—13).—The maximum alkalinity of the medium in which a Frohberg bottom yeast grew was between $P_H = 7·7$ and $P_H = 8$. A distillery top yeast (SB II) showed decided growth at $P_H = 7·3$. The maximum, however, tolerated by growing yeast depends to a great extent on the quantity of cells seeded. The maximum alkalinity for *Saccharomyces ellipsoideus* and *Pseudosaccharomyces apiculatus* was $P_H = 7·9$ and $P_H = 7·6$ respectively. The highest limit of alkalinity tolerated by *Aspergillus niger* was found to be $P_H = 9$. S. S. Z.

The Presence of Non-volatile Substances Possessing Aldehydic Properties in Yeast Macerations. J. COCHIN and R. SAZERAC (*Bull. Soc. chim. Biol.*, 1914, 1, 75—77).—The authors have observed that the maceration fluids from pressed yeast give a reddish-violet colour with Schiff's reagent. The substances which give this reaction are not volatile, so that they cannot be identified with the lower aldehydes. Their exact nature has not yet been determined. J. C. D.

Presence and Estimation of Tryptophan in Protein Material of Yeast. PIERRE THOMAS (*Bull. Soc. chim. Biol.*, 1914, 1, 67—74).—The content of tryptophan in caseinogen is approximately 1·7 to 1·8%. The protein substance from yeast, cérévisin, contains about 2·3%, and is the substance containing the highest percentage of tryptophan which is known. It also contains a high percentage of lysine, a fact which places this protein in a class by itself. J. C. D.

Invertase and Fermentation Enzymes in a Top Yeast. HANS VON EULER and E. MOBERG (*Arkiv Kem. Min. Geol.*, 1918, 7, No. 12, 1—17).—The production and the activity of the invertase of a top yeast were only influenced to a small extent by a protoplasma poison, such as chloroform. In the top yeast investigated, it was not possible to augment the invertase by Euler's method to the extent previously done in bottom yeasts. It was further found from comparative experiments with fresh yeast that, after drying it, practically the entire invertase content was retained by the dried preparation. The amount of alcohol and carbon dioxide produced from a certain quantity of sugar in alkaline solution by dried and fresh yeast was approximately the same, and was not influenced by the addition of co-enzyme. The co-enzyme, previously heated with

sodium hydroxide, became, however, more active. The authors conclude that, besides the co-enzyme and phosphate, fermentation in alkaline solution requires another activator, most probably of the nature of an alkali salt. S. S. Z.

The Behaviour of certain Dyes towards Yeast-cells. HANS VON EULER and N. FLORELL (*Arkiv Kem. Min. Geol.*, 1919, **7**, No. 18, 1—27).—Dyes are adsorbed by yeast in two ways. Some dyes penetrate the cell and are retained therein; others are adsorbed on the surface of the cell. In the former case, the cell shows the stain under the microscope; in the latter, the stain can only be detected in reflected light. The surface adsorption is the more common phenomenon of the two, and is greatly controlled by the previous preparation, especially washing, of the yeast. The adsorption in both cases is influenced by such factors as the concentration of the dye, temperature, hydrogen-ion concentration, and the presence of a fermentable sugar in the solution. The staining of yeast with chrysodine (diaminoazobenzene hydrochloride), janus-blue (safranineazo-β-naphthol hydrochloride), poncean 3R (sodium salt of cumidineazonaphtholdisulphonic acid), and methylene-blue impairs its fermenting capacity. S. S. Z.

The Culture of Aspergillus niger (Sterigmatocystis nigra, V. Tgh.) in Mediums in which Zinc is Replaced by Other Elements (Copper, Uranium, Vanadium). M. JAVILLIER (*Bull. Soc. chim. Biol.*, 1914, **1**, 55—66).—*Aspergillus niger* requires, in addition to the elements carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, potassinm, silicon, magnesium, iron, and manganese provided in suitable form, a trace of zinc. The author believes that the zinc plays the rôle of a physiological catalyst, and that it is not replaceable, in the strict sense of the word, by any of the elements examined. J. C. D.

The Aerial Fertilisation of Plants with Carbon Dioxide. M. B. CUMMINGS and C. H. JONES (*Bull.*, 1919, **211**, 56 pp.).—A number of plants were grown in boxes and frames in the greenhouse, the boxes having glass covers, and a current of carbon dioxide was kept constantly flowing into the enclosure. With legumes, the carbon dioxide caused an increased production of pods and beans and slightly changed the chemical composition of the plant by increasing the carbohydrate storage. With peas, the increase of seed yield was especially marked. Radishes responded only slightly, but were marketable soon, and contained a larger carbohydrate and smaller protein content. Potatoes produced more foliage and larger and better tubers when grown in an atmosphere of carbon dioxide. The stimulating effect was very marked with strawberries, and the growth of flowers was also better. In most cases where the plants were grown with carbon dioxide, a higher carbohydrate content was found and a lower protein content. Lettuce was most benefited when given 300 litres of carbon dioxide per day in boxes $130 \times 70 \times 30$ cm. CHEMICAL ABSTRACTS.

The Distribution of Glycerophosphatase in Seeds. ANTO NĚMEC (*Biochem. Zeitsch.*, 1919, **93**, 94—101).—Oil-bearing seec show a higher content of glycerophosphatase than do leguminoı seeds. The latter, however, are richer in this enzyme than th cereals. S. S. Z.

The Change in the Character of the Nitrogen i Germinating Lupines. The Relation of the Nitrog Titratable with Formol and the "Formalin Nitrogen to the Total Nitrogen. H. SERTZ (*Biochem. Zeitsch.*, 191 **93**, 253—255).—On the addition of neutral aqueous formaldehy to plant albumins, albuminates, and hemialbumoses, the protei become almost insoluble. This is referred to as "formal nitrogen." The author has determined the relation of the nitrog in the amino-groups which combines with formol and the "formal nitrogen" to the total nitrogen in germinated lupines at vario periods of the germination. The following are the results. Befo germination: formol nitrogen = 12·7%, "formalin nitrogen" 86·3%. After three days' germination: formol nitrogen = 18·3 "formalin nitrogen" = 82·3%. After five days: formol nitrog 24·9%, "formalin nitrogen" 70·5%. After seven days: form nitrogen 31·05%, "formalin nitrogen" 65·5%. After ten day formol nitrogen 39·4%, "formalin nitrogen" 57·6%. This demo strates the formation of soluble amino-acids at the expense of t insoluble proteins during the germination of the lupine. S. S. Z.

Germination and Formation of Chlorophyll in Confined Atmosphere deprived of Carbon Dioxide. N. BARBIERI (*Bull. Soc. chim.*, 1919, [iv], **25**, 658—661).—A coı parative study of the germination of wheat in an atmosphe deprived of carbon dioxide, in pure oxygen, and in free air, in su light and in the dark. All germination or commencement germination is marked by an elimination of carbon dioxide, wi the formation of chlorophyll in sunlight and of chromophyll the dark. In an atmosphere of pure hydrogen or nitrogen the is only a slight commencement of germination. In an atmosphe of pure carbon dioxide, germination does not take place. W. G.

The Electrometric Titration of Plant Juices. A. R. HAAS (*Soil Sci.*, 1919, **7**, 487—491).—The method used was th of the gas-chain, essentially of the form described by Hildebra (*Univ. Cal. Pub. Physiol.*, 1919, **5**, 44—69), a simplified and pla-xpensive type of apparatus being described. Measurements we it w-ade on soja bean tops and rhubarb stalk, and from the curv the ex-wing the P_H values at which various indicators change colou from co-ossible to tell the amount of standard alkali required to bri practical-nt juice to the turning point for any indicator. The cur preparatio-ow the presence of greater quantities of buffer substan from a certa-e of the rhubarb than in the juice of soja bean tops, fresh yeast w-ity of the rhubarb juice being much greater than t the addition of of soja bean tops. W. G

Hydrogen-ion Concentration of Plant Juices. I. The Accurate Determination of the Hydrogen-ion Concentration of Plant Juices by means of the Hydrogen Electrode. CLINTON B. CLEVENGER (*Soil Sci.*, 1919, **8**, 217—226).—In the method described, a Clark electrode vessel (compare A., 1916, ii, 75) modified and adapted for work with plant juices, a simple shaking apparatus, and calomel electrodes immersed in a constant temperature water-bath are used. The apparatus is so arranged that the plant juices are saturated with hydrogen outside the electrode vessel, and only come in contact with the electrodes just prior to the readings being taken. Contact between the plant juice and the saturated potassium chloride solution is made by means of a scratch around the cock connecting the two, thus reducing the contact potential, which develops quite rapidly when the connexion is made by opening the cock wide. Duplicate measurements usually agree within 0·1 millivolt, aud constant potentials are maintained for several minutes. The plant juice is prepared by macerating the tissue, wrapping it in a muslin cloth, and expressing the juice by means of a press. This gives a juice free from coarse colloidal or other material. W. G.

Hydrogen-ion Concentration of Plant Juices. II. Factors Affecting the Acidity or Hydrogen-ion Concentration of Plant Juices. CLINTON B. CLEVENGER (*Soil Sci.*, 1919, **8**, 227—242. Compare preceding abstract).—In making determinations of hydrogen-ion concentration of plant juices, certain points must be noted. Expressed plant juice usually becomes more acid on keeping, whilst plants when cut and left some time before the juice is expressed usually become more alkaline. Further, it is shown that the acidity of the leaves and stems is highest in the morning and decreases during the day, whereas the acidity of the roots is highest during the day. The decreased acidity of the leaves and stems in the day is attributed to the destruction of the accumulated acids by influences such as increased light and higher temperatures.

Oats, buckwheat, soja beans, and cowpeas were grown on acid soils and on the same soils after liming, and it was found that, with the exception of buckwheat, the tops of the plants grown on the limed soil were usually more acid than the tops of those grown on the unlimed soil. The acidity of the roots of the plants appeared to be comparable with that of the soil.

Similarly, the type of fertiliser used appears to have some influence on the acidity of plants. Thus, the acidity of the tops of oats grown on unlimed soil was less than that of those grown on limed soil when sodium nitrate or ammonium nitrate was used as a source of nitrogen. W. G.

A Method for the Macrochemical Examination of Substances contained in Cells. FRITZ NETOLITZKY (*Biochem. Zeitsch.*, 1919, **93**, 226—230).—When the finely ground powder of *Cortex quillajae* is shaken with chloroform, a sediment, con-

sisting mostly of crystals, is deposited at the bottom. These are crystals of calcium oxalate, and contain impurities such as sand grains and cell débris. The impurities can be removed by *fractional sedimentation by shaking up the deposit with chloroform*, carbon tetrachloride, or bromoform. The specific gravity of the latter can be altered by the addition of alcohol or ether. By this fractional method of differential sedimentation, a powder consisting almost of pure crystals was obtained. Such purified powder showed a content of 103·7% of CaO (calculated from the formula $CaC_2O_4 + H_2O$). By titrating the oxalic acid with permanganate, 94·8% of the theoretical amount was obtained. It is suggested that "sand" impurities were responsible for the high calcium and low oxalic acid content. From the above figures, the author also concludes that the crystals from *Cortex quillajae* have the formula $CaC_2O_4 + H_2O$. The calcium oxalate thus obtained was further decomposed with sulphuric acid. The liberated oxalic acid, which was recrystallised several times, was titrated with permanganate, and 99·23% of the theoretical value was recorded. The crystals obtained both from sesame seeds and *Saponaria officinalis* by sedimentation from carbon tetrachloride were too contaminated with organic matter to yield good results, but the low calcium content of the sediment is most probably also due to the higher water of crystallisation of the crystals. By this method, it is also possible to separate other substances, like aleurone grains, calcified membranes, etc., from powdered plants. S. S. Z.

Fixation of Calcium by Calciferous Plants. (MLLE) T. ROBERT (*Bull. Soc. chim. Biol.*, 1914, **1**, 85—92).—Calciferous plants (les plantes calcifuges) are plants which possess a marked ability to absorb calcium. They are able to live in soil deficient in calcium by virtue of this increased power of assimilation. Another class (les vegetaux calcicoles) are, on the contrary, possessed of a very low power of absorbing calcium. These require soils rich in calcium, and are able to live in the presence of an amount of calcium which would be toxic to plants of the former group.
J. C. D.

The Distribution and Migration of Copper in the Tissues of Green Plants. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, **170**, 87—93).—Copper has been shown to be present in a large number of plants and trees and in all parts of the plants. It accumulates most in the parts of the plants where there is most water and great vital activity. The parts which gradually dry up and become old gradually lose their copper, yielding it to the growing parts. The copper is thus present in a diffusible and migratory form, its migration, except in so far as amount is concerned, being comparable with that of mineral nutrients, such as potassium. The juice of all the plant organs contains copper, sometimes in comparatively large amount, sometimes only in very small amount. W. G.

Mode of Occurrence of Hydrogen Cyanide in Plants. L. ROSENTHALER (*Schweiz. Apoth. Zeit.*, 1919, **57**, 571—576. Compare this vol., i, 130).—The author destroys disturbing enzymes by 2% silver nitrate, or, preferably, 5% mercuric chloride solution, which also fixes hydrogen cyanide if present as such. Mercuric cyanide is formed, and is dissolved by potassium iodide in slight excess; hydrogen cyanide is then liberated by carbon dioxide.

The mercuric chloride method differentiates only between hydrogen cyanide in glucosidal (for example, amygdalin) and non-glucosidal (loose) combination (for example, $Ph\cdot CO_2H.HCN$), but not between the latter and free hydrogen cyanide. The silver nitrate method might do so, since silver nitrate does not at once decompose the compound, $Ph\cdot CO_2H.HCN$. Even boiling 5% mercuric chloride solution does not liberate hydrogen cyanide from amygdalin.

Hydrogen cyanide is stated to occur only combined as glucoside in bitter almonds, cherry, laurel leaves, linseed sprouts, peach leaves, *Sorghum vulgare* leaves, and the seeds of *Phaseolus lunatus*. The occurrence of hydrogen cyanide in non-glucosidal form in the buds of cherry laurel and the young leaves of *Sambucus niger* was proved by the mercuric chloride method. The leaves of *Pangium edule* and of *Alocasia macrorhiza* probably also contain hydrogen cyanide in similar loose combination. The occurrence of free hydrogen cyanide in plants has not been observed. CHEMICAL ABSTRACTS.

Distribution and Migration of Mineral Salts in an Annual Plant. G. ANDRÉ (*Bull. Soc. chim.*, 1919, [iv], **25**, 610—613).—A study of the distribution of the ash and its components in the different parts of the tall sunflower (*Helianthus annuus*) at the stage of maturity. The roots and stem contain a very small proportion of the total ash, and what is present is poor in phosphates and sulphates and rich in potassium. The leaves contain practically one half of the total ash content of the plant. This portion of the ash is very rich in lime, and comparatively so in magnesia, but very poor in potassium. The capitule contains a low percentage of ash, which is rich in phosphates and potash. The seeds contain about one-tenth of the total ash of the plant, and this portion of the ash is extremely rich in phosphates. Of the nitrogen content of the plant, about one-half is to be found in the seeds, one-quarter in the leaves, and one-eighth in the capitule. It is only in the seeds that the ash contains a higher percentage of magnesia than of lime. W. G.

Constituents of the Leaves of Helinus ovatus. JOHN AUGUSTUS GOODSON (T., 1920, **117**, 140—144).

The Inversion of Sucrose during the Preservation of Oranges. G. ANDRÉ (*Compt. rend.*, 1920, **170**, 126—128).—The amount of sucrose undergoing inversion during four months in the half of an orange kept in presence of an antiseptic appar-

ently bears no relationship to the acidity of the orange expressed in terms of citric acid. Further, the actual *inversion is much less* than that occurring in an aqueous solution of sucrose, dextrose, and citric acid, and at about the same concentrations as in orange juice kept for seventy-eight days at the ordinary temperature. Accepting Marlinand's views as to the absence of sucrose in orange juice (compare A., 1907, ii, 644), the explanation offered is that the mixture of sucrose and citric acid is not homogeneous in the orange, the two substances being localised in different cells. W. G.

The Inversion of Sucrose in Orange Juice. G. ANDRÉ (*Compt. rend.*, 1920, **170**, 292—295. Compare preceding abstract). —The hydrolysing action of the citric acid present in orange juice on the sucrose also present is very marked at the ordinary temperature. The action of the invertase present is also marked, but less intense than that of the citric acid. W. G.

Properties of Plants of the Order Polygonaceæ. A. J. STEENHAUER (*Pharm. Weekblad*, 1919, **56**, 1084—1101).—The botanical structure of the leaves of many plants of the order *Polygonaceae* is described. As regards their chemical components, no extensive research has so far been carried out, but various salts, ethereal oils, etc., have been identified in certain plants. The extraction of these from the leaves is described. Anthraquinone derivatives were found in *Polygonium convolvulus*, L., *P. dumetorum*, L., *P. Sachalinense*, Schm., *P. Sieboldii*, Hort., and possibly *P. cilinode*, Michx. For the estimation of hydroxyanthraquinone derivatives, a colorimetric method is most suitable. W. J. W.

The Flavones of Rhus. CHAS. E. SANDO and H. H. BARTLETT (*Amer. J. Botany*, 1918, **5**, 112—119).—By the isolation of flavone pigments from *Rhus typhina*, *R. glabra*, and *R. copallina*, the authors have been able to verify the conclusions of Perkin that the same flavone is not likely to be found in both the wood and leaves of the same species. Fisetin is distinctly a wood flavone, and appears to be an end-product of metabolism. It is now known to be present in *R. cotinus*, *R. rhodanthema*, *R. typhina*, and *R. glabra*. The first two species do not belong to *Rhus* in the restricted sense, but to the genera *Cotinus* and *Rhodosphaera* respectively. The authors' studies are therefore the first to demonstrate the presence of fisetin in wood of species belonging to *Rhus* proper (the true sumacs). The distinctive leaf flavone, probably a plastic substance, of *Rhus* proper is myricetin. It has been obtained from *R. Coriaria*, and the authors have been able to detect it in g*R. glabra* and *R. copallina*. The authors have not been able to ingace its relationship to the fisetin of the stem or to the anthodiffusins of the leaves and berries. Methods of extracting fisetin amonmyricetin are fully described. Colour reactions and physical nutrienties of both flavones are given, together with analytical data contains acetyl derivatives and the purified flavones.
times only CHEMICAL ABSTRACTS.

Colour Changes of Sugar-cane Juice and the Nature of Cane Tannin. F. W. Zerban (*J. Ind. Eng. Chem.*, 1919, **11**, 1034—1036).—The polyphenol present in sugar-cane juice, which gives a green coloration with ferric salts, and, together with oxydases and iron salts, is responsible for colour changes in the juice, is not catechol, but a true tannin derived therefrom. When heated alone, it produces catechol, but no pyrogallol; dilute acids give rise to a phlobaphen and protocatechuic acid, whilst fusion with potassium hydroxide yields protocatechuic and acetic acids, but neither gallic acid nor phloroglucinol. J. H. L.

Identification of Citric Acid in the Tomato. R. E. Kremers and J. A. Hall (*J. Biol. Chem.*, 1920, **41**, 15—17).—The presence of citric acid in tomato juice has been confirmed by the isolation of its triphenacyl ester. J. C. D.

The Effect of Hydrogen Cyanide on Plants. C. Wehmer (*Biochem. Zeitsch.*, 1918, **92**, 364—376).—Green cress is killed within ten days by 0·24 mg. of hydrogen cyanide per 1 litre of air. In order to achieve the same effect with seeds placed in water, 71·3 mg. of the acid per litre of air are required, although 2·375 mg. of the poison per litre of air greatly impair their germination and development. Green leaves submerged in water are also killed by very dilute solutions of hydrocyanic acid. S. S. Z.

The Influence of Arsenious Acid on Growing Tissues. Rudolf Cobet (*Biochem. Zeitsch.*, 1919, **98**, 294—314).—The influence of arsenious acid on various plants and lower animals was studied. In the plants, no improvement in the growth was observed by the application of arsenious acid. Concentrations of 1/200,000 were found to be very toxic. Frogs' spawn and tadpoles were not so susceptible to the toxic effect of arsenious acid, but neither improvement nor retardation in growth of these organisms could be traced to the influence of the arsenic compound.
S. S. Z.

Enzymes. I. Amylase of Germinated Barley. D. Maestrini (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 393—394).—A highly active amylase solution may be obtained by extracting germinated barley with water containing 0·003 mol. % of acetic acid for at least six hours. [See, further, *J. Soc. Chem. Ind.*, 1920, March.]
T. H. P.

Enzymes. II. Protease and Lipase of Germinated Barley. D. Maestrini (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 456—458).—The protease and lipase of germinated barley are not extractable by water, being found, not in the filtrate, but only in the residual emulsion. If distilled water is used for the extraction, the emulsion shows no proteolytic, and but slight lipolytic, activity; if, however, the water contains 0·003 mol. % of acetic acid, the emulsion *exhibits*

both activities to a marked extent. [See, further, *J. Soc. Chem. Ind.*, 1920, March.] T. H. P.

Fat-soluble Vitamine. III. The Comparative Nutritive Value of White and Yellow Maize. H. STEENBOCK and P. W. BOUTWELL [with the co-operation of E. G. GROSS and MARIANA T. SELL (*J. Biol. Chem.*, 1920, **41**, 81—96).—The occurrence of yellow pigment and the growth-promoting property attributed to the presence of the fat-soluble vitamine seem to be intimately associated in the maize kernel. J. C. D.

Activity of Soil Acids. R. E. STEPHENSON (*Soil Sci.*, 1919, **8**, 41—59).—Using a modification of Tacke's method, previously described (*ibid.*, 1918, **6**, 33), an endeavour has been made to arrive at the degree of activity of the soil acids, the lime requirements being determined by allowing different times of contact for the soil and calcium carbonate. It is shown that the more reactive acids, which are capable of giving a toxic hydrogen-ion concentration, react rather quickly, but that some soils contain a large reserve of activity, which may be described as potential rather than active, but which is, however, capable of slowly decomposing carbonates. Rather highly buffered solutions react rapidly with calcium carbouate, even in the presence of soil, thus indicating that even the more active fractions of the soil acids may be considerably buffered. So far as tested, protein materials and amino-acids, previous to decomposition in the soil, do not react readily with carbonates. The author considers that the total potential acidity of a soil, as commonly determined, does not give sufficient information. It is necessary also to know something of the activity of the acids. It is not the capacity of a soil to decompose calcium carbonate, but rather the intensity of decomposition which is most highly significant.

In a discussion on the origin of soil acidity, the development of an acid condition in soils is considered from three points of view, namely, mineral acids, organic acids, and colloids. The weathering of rocks tends to give acid alumino-silicates and silicic acids, resulting in a comparatively large reserve of slowly reactive acids. Toxic acid reactions are, however, more probably due to the presence of more soluble and highly ionised acids, such as sulphuric, hydrochloric, or nitric acids, generally introduced by the application of fertilisers. It is only occasionally, and in highly organic, badly drained soils, that organic acids accumulate to a detrimental extent; in fact, in some soils organic matter may quite likely depress the more active acidity by buffering and by supplying a base in the form of ammonia and its derivatives. W. G.

Hysteresis of Aqueous Solutions of Humus Earth. HEINRICH PUCHNER (*Kolloid Zeitsch.*, 1919, **25**, 196—207).—An examination of peat shows that a clear, dark yellow solution may be obtained by digesting it with cold water. During the solution,

a faintly acid, somewhat aromatic odour is noticeable. The solution obtained has an acid reaction, and, on keeping for several days, deposits a slimy, brown substance, and the clear solution then becomes alkaline. The deposit from the solution obtained from 50 grams of peat amounts to 0·490 gram, and, on incinerating this, a residue of 0·218 gram is obtained. The ignited residue contained alumina, ferric oxide, manganese oxide, lime, magnesia and alkalis, sulphate, silicate, and phosphate. The solution and the deposit were examined microscopically immediately after preparation and after measured intervals, and it is shown that, after keeping for some time, changes occurred in them, notably the formation of crystals. The clear solution after sedimentation is shown to contain gels of alumina, ferric hydroxide, and silicic acid. Microphotographs of the various preparations are reproduced in the paper. J. F. S.

The Carbonation of Burnt Lime in Soils. WALTER HOGE MACINTIRE (*Soil Sci.*, 1919, **7**, 325—453).—A detailed study of the rate and manner of carbonation of calcium oxide and hydroxide, as such, or when mixed with soil under various conditions.

Dry calcium oxide or hydroxide does not react with dry carbon dioxide, but a very small amount of water suffices to start the action. The ignition of calcium hydroxide gives an oxide which, in small quantities, carbonates more rapidly when exposed to moist air than does the original hydroxide. The formation of carbonate from the hydroxide is controlled by the amount of free water available to convert the calcium hydroxide from solid to solution phase. The conversion of calcium oxide to the carbonate must be preceded by the formation of the hydroxide and its solution, but when moist carbon dioxide is present the two actions are so rapid as to be considered as simultaneous. The carbonation of calcium hydroxide in atmospheric exposure tends to be checked after a time by the formation of a protecting film-coating of carbonate round included nuclei of the hydroxide.

The general conclusions to be drawn from the extensive pot and field trials are as follows: Calcium oxide or hydroxide when applied at the rate of 2—4 tons per acre will revert to the carbonate more rapidly when left on the soil surface than when mixed with a dry mulch or the moist soil, the reversion being most rapid during humid atmospheric conditions. If a dressing of the oxide or hydroxide is left on the surface for several days prior to incorporation with the soil, the treatment is in effect equivalent to an application of finely divided calcium carbonate. If the oxide or hydroxide is incorporated with the top layer of soil, prior to a more thorough dissemination throughout the soil, the concentration may be sufficient to effect a temporary, partial sterilisation in this layer, which may have beneficial results. The first action of the calcium oxide applied to the soil is with the atmospheric and soil moisture, and there is no indication, when this is completed, of any tendency

to cause chemical disintegration of soil organic matter. Neither calcium oxide nor hydroxide, when applied in the amounts commonly used in practice, can be considered as chemically destructive of soil organic matter. [See, further, *J. Soc. Chem. Ind.*, 1920, 124A.] W. G.

Calcium Cyanamide and Dicyanodiamide as Vegetation Factors. EDUARD LINTER (*Inaug. Diss.*, 1917; from *Bied. Zentr.*, 1919, **48**, 414—417).—In contact with sand or clay in presence of carbon dioxide, dicyanodiamide solution undergoes no change, but humous soils are able to absorb the dicyanodiamide with avidity, the poisonous effect on vegetation gradually disappearing. [See also *J. Soc. Chem. Ind.*, 1920, 166A.] T. H. P.

Prevention of Volatilisation of Ammonia by means of Calcium Chloride. A. STUTZER (*Fühling's Landw. Zeit.*, 1919, **68**, 59—63).—Five grams of a sulphate or chloride of an alkali or alkaline earth metal were boiled for fifteen minutes with 250 c.c. of ammonium carbonate solution containing 0·25 gram of nitrogen; the percentage of ammonia which was volatilised was 77 with potassium, sodium, or calcium sulphate, 80 with magnesium sulphate, 87 with potassium chloride, 88 with sodium chloride, 83 with magnesium chloride, and 17 with calcium chloride. Five % of the ammonia volatilised from a solution of ammonium chloride which was exposed with calcium carbonate to the air for twelve days. The addition of 2 parts, 4 parts, and 6 parts of calcium chloride to 1 part of a volatile ammonium salt prevents 25, 50, and 75%, respectively, of the ammonia from volatilising; to preserve 90% or more of the ammonia, 8 parts of calcium chloride must be added for 1 part of nitrogen. Good results are secured when 6 parts of calcium chloride, which is a better conserving medium than gypsum, are added to urine for every 1 part of nitrogen.

CHEMICAL ABSTRACTS.

Guano from Sardinia. M. GIUA (*Gazzetta*, 1919, **49**, ii, 246—249).—The author has analysed a number of samples of bat guano from the Borutta grotto at Sassari, Sardinia. Streaks or veins of a white, friable material, greasy to the touch, occur in the guano, particularly in that of recent origin; this consists of tricalcium phosphate, together with calcium carbonate, silica, oxides of iron, aluminium and magnesium, and small proportions of nitrates, and resembles ordinary phosphorite, being formed by the action on the calcium carbonate of the surrounding rock either of the phosphoric acid present in freshly formed guano or of ammonium phosphate. The occurrence of this material in the guano is regarded as confirmation of the view that many phosphatic deposits owe their origin to deposits of guano. T. H. P.

Organic Chemistry.

Low Temperature Carbonisation. FRANZ FISCHER and W. GLUUD (*Ber.*, 1920, **53**, [*B*], 250—251).—The authors maintain their scientific and technical priority (compare A., 1919, i, 377) against Tern (this vol., i, 1). H. W.

The Interaction of Chlorine and Marsh Gas under the Influence of Light. The Conversion of Methyl Chloride into Methyl Alcohol and Methyl Acetate. JOHN REGINALD HARVEY WHISTON (T., 1920, **117**, 183—190).

Derivatives of Pentanes from Petroleum and certain of their Homologues. OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1915, **58**, pp. 122; from *Chem. Zentr.*, 1918, ii, 939—941).—An account is given of the action of chlorine on the paraffins and of other substances prepared from the chloro-derivatives. The chief products investigated are the pentane mixture, b. p. 30—38°, a hexane, and a fraction, b. p. 10—12°, obtained during distillation of the pentanes. Starting from *iso*pentane, $CHMe_2Et$, it has been found possible to synthesise completely the main constituents of fusel oil, namely, the two primary *iso*amyl alcohols, *iso*butylcarbinol and *sec.*-butylcarbinol, which can thus be prepared cheaply and in unlimited quantity, since *iso*pentane occurs abundantly in all known mineral oils. The application of *iso*pentane and other suitable hydrocarbons from mineral oils (*n*-butane, *n*-pentane, and various hexanes, particularly $\beta\gamma$-dimethylbutane) to the preparation of isoprene and its homologues has been investigated. It is found that all the *iso*pentyl chlorides, certain of them therefore under isomerisation, lose hydrogen chloride under suitable conditions, with the formation of β-methyl-Δ^{β}-butylene; the latter unites with chlorine in definite circumstances to yield the corresponding dichloride, which is converted by the action of bases into isoprene. It is also found that the dichloro*iso*pentanes, obtained by direct chlorination of the hydrocarbon, and probably containing β-methyl-Δ^{β}-butylene chloride, lose hydrogen chloride at a sufficiently high temperature and yield isoprene.

I. *Derivatives of* iso*Pentane.*—Dry chlorination of *iso*pentane yields a mixture of the four *iso*pentyl chlorides, together with dichlorides, which are interesting on account of their relationship to isoprene. *δ-Chloro-β-methylbutane* has b. p. 99—102°, D_{15}^{15} 0·8692; *α-chloro-β-methylbutane*, b. p. 96—99°, D_{15}^{15} 0·8818; *γ-chloro-β-methylbutane*, b. p. 90—93°, D_{15}^{15} 0·8752; *β-chloro-β-methylbutane*, b. p. 85·5—88°, D_{15}^{15} 0·8692. *β-Methylbutyl acetate*, prepared from the corresponding *iso*amyl chloride, potassium acetate, and acetic acid at 190—200°, has b. p. 140—142°, D_{15}^{15} 0·8720, and, on hydrolysis, gives the corresponding *iso*amyl alcohol, b. p. 128·5—129·5°/

772 mm. *δ-Methylbutyl acetate* has b. p. 139—142°, and is converted by alcoholic potassium hydroxide into *γ-methylbutyl alcohol*, b. p. 130—133°. The constitution of the alcohols is decided by oxidising them to the corresponding valeric acids. β-Methyl-Δ^{β}-butylene (in addition to very little acetate) is the main product of the action of potassium acetate on *sec.-iso*amyl chloride and the sole product obtained from *tert.-iso*amyl chloride. For purposes of comparison, the latter was prepared by the action of hydrogen chloride on methylbutylene in anhydrous ether; it was found to be the sole product of the change, and to be entirely reconverted into methylbutylene by removal of hydrogen chloride. Attempts are described to obtain the *iso*pentyl acetates by the use of alcoholic potassium acetate, and it is found that the *iso*amyl chloride from fusel oil (containing much primary *iso*amyl chloride and little primary active *iso*amyl chloride, and therefore consisting of the most difficultly decomposed *iso*pentyl chlorides) is converted at 200° completely into amyl acetate and amyl alcohol. Moist chlorination of *iso*pentane leads to the production of small quantities of *sec.-iso*amyl chloride, large amounts of primary *iso*amyl chloride and primary active *iso*amyl chloride, and no *tert.-iso*amyl chloride. The best yields of monochloropentanes are obtained from light petroleum when it is subjected to dry chlorination, and it is found that *n*-pentane is less easily acted on than is *iso*pentane. The mixture of monochlorides obtained from *iso*pentane behaves towards alcohol and potassium acetate in the same manner as *iso*pentyl chloride from fusel oil. *iso*Pentyl chloride does not react with 2% potassium hydroxide solution at 60—70°. Only slight transformation occurs when *iso*amyl chloride is heated at 250°, more marked, but still incomplete, change at the same temperature in the presence of concentrated hydrochloric acid. Further chlorination of *tert.-iso*amyl chloride gives β-methyl-Δ^{β}-butylene chloride in unsatisfactory yield; the product which is thus obtained, as also the dichloride prepared by the direct chlorination of *iso*pentane, yields isoprene when heated with reagents which remove hydrogen chloride at 300—400°.

When the vapours of fermentation amyl alcohol are led over aluminium hydroxide impregnated with finely divided copper and heated at dull redness, β-methyl-Δ^{β}-butylene is mainly formed. Regulated chlorination of the latter gives mainly *iso*amylene chloride, CH_2:CMe·CHMeCl, and but little dichloride; probably a second chloroamylene, possibly CMe_2Cl·CH:CH_2, is also formed. The fraction, b. p. 90—100°, and the dichloride can be used in the preparation of isoprene. Different products are obtained when hydrogen bromide is removed from methylbutylene bromide by different bases. Elimination of both bromine atoms only occurs incompletely; β-bromo-γ-methyl-Δ^{α}-butylene is obtained in the pure condition by the use of alcoholic potassium hydroxide. Unsuccessful attempts are described to prepare the corresponding glycol by the oxidation of β-methyl-Δ^{β}-butylene with potassium permanganate.

The author describes experiments on the distillation of caoutchouc and *on the conversion of isoprene* obtained by heating the vapour of turpentine oil into its derivatives. The process first named yields only 1·9% of crude isoprene and 13% of a hydrocarbon (? terpene), b. p. 170—175°, which has not been more closely investigated. Pyrogenic decomposition of turpentine gives about 5% of crude isoprene, b. p. 30—40°; in the fraction b. p. up to 100°, at least two further hydrocarbons are found, one of which, b. p. ca 70°, occurs in particularly large amount and is unstable towards permanganate; the fractions of higher b. p. contain undecomposed terpenes, benzene, and its simpler homologues. The crude isoprene is purified by conversion into βδ-dibromo-β-methylbutane, b. p. 67°/9 mm., from which it is regenerated by potassium hydroxide; the pure isoprene has b. p. 34—34·5°/758 mm., D_{15}^{15} 0·6848, D_4^{20} 0·6811, n_D^{20} 1·41540. Experiments are also described on the conversion of technical crude isoprene into already known isoprene derivatives. It is found that not only amylene, but also all hydrocarbons which contain at least one true ethylenic linking, can be condensed with isoprene by means of aluminium chloride to yield similar condensation products. Conversely, hydrocarbons other than isoprene, which contain two conjugated double bonds, can be condensed with amylene and other singly unsaturated hydrocarbons. Variation of the relative amount of amylene and isoprene causes variation in the composition of the products. The author claims to have discovered the condensing action of sodium on isoprene independently of, and simultaneously with, Harries and Matthews; he obtained from crude isoprene and sodinm a product, insoluble in alcohol but soluble in ether, which he terms "semicaoutchonc," which can be vulcanised. Sodium has no action on pure β-methyl-Δ^{β}-butylene. Pure isoprene, when heated alone during thirteen days, was less completely polymerised than after three days in the presence of sodium. Experiments on polymerisation by *metallic oxides* and *on vulcanisation of semicaoutchouc* are also described.

II. *Experiments with* n-*Pentane from Petroleum.*—A second n-*pentyl chloride*, b. p. 96—98°, is formed in addition to the previously described α-chloropentane, b. p. 106·6°, by the chlorination of *n*-pentane obtained from petroleum; an *iso*pentane derivative is not produced.

III. *Examination of Petroleum Fraction*, b. p. 10—12°.—When the fraction is chlorinated in the presence of water, the main product is a chloride, C_4H_7Cl, b. p. 69—70°, thus showing that it consists mainly of a butane; the presence of *iso*butane could be definitely established, but *n*-butane appears either to be absent or present in small quantity. The b. p. of *iso*butane has been given as −17°, but this can scarcely be correct. It is remarkable that, whilst the naturally occurring fatty acids have a normal carbon chain, the hydrocarbons obtained from petroleum have, in general, branched chains.

IV *Certain Hexane Derivatives from Petroleum.*—Preliminary

experiments on the chlorination of a hexane fraction, b. p. 58—60°, and consisting chiefly of diisopropyl, led to the identification of both the possible monochloro-derivatives of this hydrocarbon, together with a third monochlorohexane, the constitution of which has not been elucidated. H. W.

Oxidation of Hydrocarbons by Oxygen. Oxidation of Paraffin. C. KELBER (*Ber.*, 1920, **53**, [*B*], 66—71).—Paraffin, vaselin, petroleums, and the higher fatty acids may be rapidly oxidised by submitting them to the action of finely divided streams of oxygen at 140—150°, especially in the presence of manganese compounds. In the case of a paraffin with m. p. 50—51°, 25% of the product was a distillate, consisting of oil and aqueous solution, in which acetone, formic, acetic, propionic, butyric, valeric, hexoic, octoic, nonoic, and decoic acids were identified. The pasty residue contained 40—50% of fatty acids insoluble in water, but soluble in light petroleum, and 5—10% of acids insoluble in petroleum.
J. C. W.

Nitration of Ethylene. HEINRICH WIELAND and EUKLID SAKELLARIOS (*Ber.*, 1920, **53**, [*B*], 201—210).—The hypothesis has been advanced by Thiele and elaborated by Holleman that substitution in the benzene series is preceded by addition, and that the primary reaction is similar in the ethylene and benzene series; in the former case the additive products, however, are stable, whilst in the latter, rearrangement immediately occurs, with the production of a more stable system. A certain amount of experimental evidence is available in the instances of halogenation and sulphonation, but very little work has been done on the nitration of ethylenic substances. The authors have therefore studied the behaviour of ethylene towards nitrating acid, and have shown that, under suitable conditions, ethylene dinitrate and nitroethyl nitrate are produced; it would thus appear that reaction is primarily additive in character, and results in the formation of β-nitroethyl alcohol, which, under the experimental conditions, is further esterified.

Ethylene is passed through an ice-cold mixture of nitric acid (D 1·4) and concentrated sulphuric acid containing 20% of sulphur trioxide, and the products are separated by distillation with steam and subsequent careful fractionation under diminished pressure; ethylene dinitrate, colourless oil, b. p. 105·5°/19 mm., D^{17} 1·433, and *β-nitroethyl nitrate*, colourless, poisonous oil, b. p. 120—122°/17 mm., D^{18} 1·468, are thus isolated. The latter is converted by phosphoric oxide into nitroethylene (compare A., 1919, i, 307).

Discrepancies between the properties of specimens of β-nitroethyl alcohol obtained by the authors and those described by V. Meyer and Henry have led them to examine in greater detail the action of silver nitrite on ethylene iodohydrin; it is found that the substance which is thus prepared is contaminated with ethylene glycol mononitrite, which can be removed by careful fractionation, and

with ethylene glycol, which cannot be thus removed, but is readily eliminated by washing the product with water. Pure β-nitroethyl alcohol is a colourless, odourless liquid, b. p. 103°/11·5 mm., $D^{13.3}$ 1·309; it is miscible in all proportions with water, alcohol, and ether. The aqueous solution does not give a coloration with ferric chloride, and the ketonic form can only be detected for a few seconds with this reagent after cautious acidification of the sodium salt. Contrary to Henry's observations, it cannot be distilled at the ordinary pressure, since it is thereby decomposed into water and nitroethylene.

Attempts to isolate nitroacetaldehyde in substance have not been successful up to the present; if, however, a mixture of β-nitroethyl alcohol and sulphuric acid is added to a boiling suspension of lead peroxide in water and the distillate is treated with o-nitrophenylhydrazine hydrochloride, *nitroacetaldehyde-o-nitrophenylhydrazone*, slender, orange-red needles, m. p. 83·5°, is obtained.

H. W.

Preparation of Propylene. ARTHUR HEINEMANN (D.R.-P. 315747; from *Chem. Zentr.*, 1920, ii, 186).—Acetylene is caused to unite with methane in the presence of contact substances consisting of mixtures of noble metals (platinum, iridium, and palladium) and common metals (iron, nickel, copper, silver, aluminium). The technical preparation of the contact agent is effected by depositing the common metal, such as copper, either electrolytically or by purely chemical reduction of a copper salt on a porous material, such as pumice; the latter is placed in a solution of a noble metal (for example, platinous chloride), dried, and, if necessary, again reduced. Methane is completely utilised at 100—200° if an excess of acetylene is employed. The heating may be replaced by the chemically active violet or ultra-violet rays, or by the silent electric discharge. The yield of propylene is 70% of that theoretically possible.

H. W.

The Action of Nitric Acid on Unsaturated Hydrocarbons. The Action of Nitric Acid on Acetylene. KENNEDY JOSEPH PREVITÉ ORTON and (MISS) PHYLLIS VIOLET MCKIE (T., 1920, **117**, 283—296).

Preparation of Methyl Chloride and Bromide from Methyl Sulphate. CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1920, **170**, 595—597).—Methyl chloride may readily be prepared in a very pure state and with an excellent yield by allowing methyl sulphate to drop into hydrochloric acid (D 1·112) at about 50°, the change occurring being represented by $Me_2SO_4 + HCl = MeHSO_4 + MeCl$. The hydrochloric acid may be replaced by a concentrated solution of sodium chloride, but in this case a slightly higher temperature is necessary.

In the same way, methyl bromide may be obtained by letting

methyl sulphate drop into hydrobromic acid at 45—50°, or, preferably, *into a concentrated solution of an* alkali bromide, *slightly* acidified with sulphuric acid, at 30—35°. W. G.

Organic Chemical Reagents. V. The Preparation of Alkyl and Alkylene Bromides. OLIVER KAMM and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1920, **42**, 299—309).—A detailed study has been made of the preparation of *n*-butyl bromide from the corresponding alcohol by the hydrobromic acid method; addition of sulphuric acid to the reaction mixture was found to be of more value than an increase in the quantity of hydrobromic acid. The effectiveness of sulphuric acid does not depend entirely on the resulting removal of water from the reaction mixture, but is also to be explained by the formation of an alkyl hydrogen sulphate, which probably reacts more readily with hydrobromic acid; the effect of sulphuric acid in preventing the distillation of alcohol from the reaction mixture is also an important factor.

The Norris-Bodroux method for the preparation of primary alkyl bromides has been modified in the following manner. The alcohol is treated with a 25% excess of aqueous hydrobromic acid, together with sulphuric acid. The mixture is heated under reflux in order to convert the alcohol as completely as possible into the corresponding bromide, and the latter is then removed from the reaction mixture by direct distillation. Slight variations from this procedure depend on the physical and chemical properties of the alcohol used or of the bromide formed in the reaction. For example, in the preparation of ethyl and allyl bromides, the mixture is not heated under reflux, because of the volatility of the former compound and the chemical reactivity of the latter; in the preparation of *iso*amyl bromide, a somewhat smaller proportion of sulphuric acid is used in order to prevent charring: haloids of high molecular weight, because of their high boiling points, are separated from the reaction mixture mechanically instead of by distillation. Detailed directions are given for the preparation of the following compounds, the corresponding yields being enclosed within brackets: *n*-butyl bromide, b. p. 101—104° (95—97%); *iso*amyl bromide, b. p. 116—120° (88—90%); trimethylene bromide, b. p. 162—165° (88—95%); trimethylene chlorobromide, b. p. 142—145° (89%); ethyl bromide, b. p. 38—40° (90—95%); allyl bromide, b. p. 69—72° (92—96%); *n*-octyl bromide, b. p. 196—200° (91%); lauryl bromide, b. p. 175—180°/45 mm. (91%).

The requisite hydrobromic acid solution is conveniently prepared by the reduction of bromine by sulphur dioxide in the presence of water; the mixture may be utilised directly without a preliminary distillation, the necessary additional quantity of sulphuric acid being added as concentrated acid.

Mixtures of constant boiling hydrochloric and hydrobromic acids, such as are obtained when alkyl bromides are used with aluminium chloride in Friedel-Crafts' reactions, may be separated readily by fractional distillation. H. W.

Gaseous Methyl Fluoride. I. Revision of the Atomic Weight of Fluorine. E. MOLES and T. BATUECAS (*J. Chim. Phys.*, 1919, **17**, 537—588).—The methyl fluoride was prepared either by heating together methyl potassium sulphate and potassium fluoride or by passing the vapour of methyl iodide over anhydrous silver fluoride at 90°. The weight of a normal litre of methyl fluoride was found to be 1·5454 grams, whilst measurements made at 506·67 mm. and 253·33 mm. indicate that the departure from Avogadro's law is given by $1+\lambda=1\cdot0181$, and the coefficient of compressibility of methyl fluoride is 0·000037 per mm. The weight of a normal litre of oxygen under similar conditions was 1·4293, hence the molecular weight of methyl fluoride is 34·021 and the atomic weight of fluorine is 18·998.

Measurements of the vapour pressure of methyl fluoride between −77° and −105° give as its b. p. −78·2°/760 mm. The molecular heat of vaporisation, calculated by the Clausius-Clapeyron formula, is $\lambda=4361$ cal., and from this the Ramsay-Trouton constant is found to be 22·4. The critical temperature deduced by the Guldberg-Guye rule is $T_c=325\cdot3°$.

In the preparation of methyl fluoride by the action of methyl iodide on silver fluoride, a brick-red compound is formed, which has the composition 2AgF,AgI. W. G.

The Dehydrogenation of Primary and Secondary Alcohols by Catalytic Oxidation. General Method of Preparation of Aldehydes and Ketones. CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1920, **170**, 258—261).—Finely divided silver, deposited on asbestos by precipitation from silver nitrate with formaldehyde, is an excellent catalyst for the oxidation of primary and secondary alcohols to aldehydes and ketones respectively. The vapour of the alcohol, mixed with slightly less than the theoretical amount of air, is passed over the catalyst heated at 230—300°. In some cases the action is so intense as to cause very marked local rise in temperature of the catalyst, and consequent destruction of some of the products of oxidation. In this case, it is better to conduct the operation in two stages. First pass the alcohol vapour, mixed with 40—50% of the requisite amount of air, over the catalyst, and then mix the issuing vapours with the other 50% of air and pass the new mixture over a second lot of the catalyst. Good results were obtained with methyl, ethyl, butyl, amyl, allyl, benzyl, cinnamyl, *iso*propyl, and secondary butyl alcohols by this method. W. G.

Organic Chemical Reagents. VI. Reagents from *n*-Butyl Alcohol. ROGER ADAMS and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1920, **42**, 310—320).—The discovery of the method by which starch may be fermented to give acetone and *n*-butyl alcohol has caused the latter substance to become available in large quantity at a low price. The authors show it to be a valuable material for the preparation of *n*-amyl derivatives and *n*-hexoic

acid and its derivatives. Detailed instructions are given for the preparation of the following substances, the yields being placed within brackets: *n*-butyl bromide (this vol., i. 282); *n*-butyl cyanide, b. p. 138—141°, from the bromide and sodium cyanide in aqueous-alcoholic solution (75—80%); *n*-valeric acid, b. p. 183—186°, from butyl bromide and sodium cyanide, and hydrolysis of the crude product with sodium hydroxide (81%); ethyl *n*-valerate, b. p. 142—146°, from *n*-butyl cyanide, ethyl alcohol, and sulphuric acid (85—90%); *n*-amylamine, b. p. 102—105°, by addition of a solution of *n*-butyl cyanide in alcohol to a suspension of sodium in toluene (57—68%); *n*-amyl alcohol, by reduction of ethyl *n*-valerate by sodium in the presence of alcohol (56—61%); ethyl *n*-butylmalonate, b. p. 144—145°/40 mm., 235—240°/ordinary pressure, from *n*-butyl bromide and ethyl sodiomalonate (89—92%); *n*-hexoic acid, b. p. 200—205°, by hydrolysis of ethyl *n*-butylmalonate with potassium hydroxide, acidification of the solution with hydrochloric acid, and subsequent distillation (74%); α-bromohexoic acid, b. p. 148—153°/30 mm., by bromination of *n*-butylmalonic acid and elimination of carbon dioxide from the product (71%); α-aminohexoic acid, from the α-bromo-acid and ammonia (65%). H. W.

Synthesis of Tertiary α-Keto-alcohols: Correction. D. GAUTHIER (*Compt. rend.*, 1920, **170**, 325).—It has previously been indicated that cyanohydrins of the type $HO\cdot CR^1R^2\cdot CN$ react with organo-magnesium haloids, R^3MgX, to give α-ketonic tertiary alcohols, $HO\cdot CR^1R^2\cdot COR^3$ (compare A., 1911, i, 513). It has since been found that the main product of such a reaction is the tertiary alcohol, $CR^1R^2R^3\cdot OH$. Consequently, the substance previously described as acetyldimethylcarbinol, $CH_3\cdot CO\cdot CMe_2\cdot OH$, is really trimethylcarbinol, and the two substances described as propionyldimethylcarbinol, $C_2H_5\cdot CO\cdot CMe_2\cdot OH$, and acetylmethylethylcarbinol, $CH_3\cdot CO\cdot CMeEt\cdot OH$, are really dimethylethylcarbinol. W. G.

Catalytic Preparation of Ethers in the Dry Way. A. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1920, [iv], **27**, 121—126; *Compt. rend.*, 1920, **170**, 329—331).—Using the method previously described for the catalytic preparation of ethyl ether (this vol., i, 6), calcined alum being the catalyst, the authors have succeeded in preparing a number of simple and mixed aliphatic ethers from the corresponding alcohols up to *iso*amyl alcohol. *iso*Propyl alcohol and *iso*butyl alcohol only gave very small yields of the corresponding ethers. W. G.

Action of Water on Methyl Chlorosulphonate. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1920, **170**, 326—328).—The action of water on methyl chlorosulphonate depends on the relative

amounts of water and sulphonate present. The action is complex and is regulated by three changes, thus:

$$SO_2Cl\cdot OMe + 2H_2O = H_2SO_4 + HCl + MeOH,$$
$$SO_2Cl\cdot OMe + H_2O = H_2SO_4 + MeCl,$$
$$SO_2Cl\cdot OMe + H_2O = HMeSO_4 + HCl,$$

with which, under some conditions, are joined the actions:

$$HCl + MeOH = MeCl + H_2O,$$
$$HMeSO_4 + MeOH = H_2SO_4 + Me_2O.$$

The primary change is the one which produces methyl hydrogen sulphate, which is, in its turn, decomposed by an excess of water to give sulphuric acid and methyl alcohol. The latter change is limited by the reverse action, but for a large excess of water the proportion of methyl hydrogen sulphate remaining is small and independent of the amount of water.

When the amount of water diminishes, the concentration of the acids becomes important, the esterification of the methyl alcohol becomes of main importance, and consequently a more and more marked synthetic production of methyl chloride occurs. W. G.

Action of Water on Methyl Sulphate. CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1920, **170**, 392—394).—If a large excess of water acts on methyl sulphate for a relatively short time, a unimolecular reaction occurs, thus: $Me_2SO_4 + H_2O = MeHSO_4 + MeOH$.

If the proportion of sulphate to water is 1:10, at the end of twenty-four hours a second action is noticeable, $Me_2SO_4 + H_2O = H_2SO_4 + Me_2O$, and this action becomes preponderant. At the same time, a secondary change may occur, $Me_2SO_4 + MeOH = MeHSO_4 + Me_2O$.

Methyl sulphate is, however, soluble in water at 18° to the extent of 28 grams per litre, this solubility being modified by the accumulation of the sulphuric acid and methyl ether resulting from the above changes. W. G.

The Sulphochromic Combustion of Methyl Esters. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1920, **170**, 514—516).—The esters were oxidised by chromic anhydride in the presence of sulphuric acid, the carbon dioxide liberated being collected in a Bunte burette and measured. In some cases, the reacting mixture required heating in a water-bath. Satisfactory results were obtained with all the esters tried. The change apparently takes place in two stages, methyl hydrogen sulphate being first formed, $R\cdot CO_2Me + H_2SO_4 \rightleftharpoons R\cdot CO_2H + MeHSO_4$, and oxidation then occurring.

Under similar conditions, ethyl esters undergo little or no oxidation, except in those cases where the organic acid radicle is readily oxidised, in which case ethyl hydrogen sulphate is formed and the organic acid is oxidised.

Substituted radicles, whether methyl or ethyl, do not underg oxidation at all readily. Thus, methyl malonate is readily oxidised but with methyl methylmalonate the oxidation is very incomplete
W. G.

ββ'-Dichloroethyl Sulphide. CHARLES STANLEY GIBSON and (SIR) WILLIAM JACKSON POPE (T., 1920, **117**, 271—278).

A Synthesis of ββ'-Dichlorodiethyl Sulphide (Mustard Gas). J. E. MYERS and H. STEPHEN (*J. Soc. Chem. Ind.*, 1920, **39**, 65T).—By passing pure ethylene into cooled sulphur dichloride until no further absorption takes place, a product containing 65% of mustard gas with 20—25% of sulphur monochloride is obtained. The formation of the latter compound, together with the evolution of considerable quantities of hydrogen chloride, is probably due to the decomposition of sulphur dichloride into the monochloride and chlorine, which then chlorinates the mustard gas. This secondary reaction is best avoided by spraying the dichloride (a mixture of 75% dichloride and 25% monochloride being most suitable) by means of compressed ethylene into an atmosphere of ethylene. In this manner, a product containing 93% mustard gas is obtained.

A solution of sodium hypochlorite containing sodium hydrogen carbonate was found to remove mustard gas almost immediately from the surface of shells. J. K.

ββ'-Dichloroethyl Sulphide. P. SPICA (*Gazzetta*, 1919, **49**, ii, 299—302; *Boll. chim. farm.*, 1919, **58**, 361—363).—The author has prepared ββ'-dichloroethyl sulphide by a method which is not described, but is simpler than that originally used by V. Meyer. This compound forms long, silky, white needles, m. p. 10—11°, b. p. 180—185°/20—25 cm., 215—217° (decomp.); in the liquid state it has D^{15} 1·275, and is colourless, its odour recalling that of garlic. It is an oxidisable compound, and on this property depends the use of calcium hypochlorite, potassium permanganate, etc., to neutralise its effects. Concentrated nitric acid acts slowly on it and yields varying results, but the action of 30% hydrogen peroxide solution in glacial acetic acid gives first the sulphoxide,

$$(CH_2Cl\cdot CH_2)_2SO,$$

m. p. 50—52°, which acts as an irritant on the eyes and skin, especially when vaporised from solution, and afterwards the sulphone, $(CH_2Cl\cdot CH_2)_2SO_2$, m. p. 110°, which is almost non-volatile in a current of steam and exerts no irritating action.

Of the various reagents proposed for the detection of ββ'-dichloroethyl sulphide, the only one which is specific is sodium iodide, this giving the corresponding di-iodo-compound. The presence of vapour of the sulphide in the air may also be detected by the formation of the sulphone occurring when the air is passed through a glacial acetic acid solution of hydrogen peroxide (see above), and also by the white turbidity, due to the formation of Meyer's non-

resolvable diethylene disulphide, produced when the air is passed through a narrow tube into hot sodium sulphide solution.

T. H. P.

Synthetical Experiments with ββ′-Dichloroethyl Sulphide. WILLIAM DAVIES (*T.*, 1920, **117**, 297—308).

***iso*Amylsulphonium Compounds.** RUDOLF WEGSCHEIDER and HELENE SCHREINER (*Monatsh.*, 1919, **40**, 325—339).—Only a slight quantity of sulphonium compound was produced by the interaction of *iso*amyl iodide with di*iso*amyl sulphide for five months. This was not due to steric influences, since, although the velocities of combination of the sulphide with methyl, ethyl, and *iso*amyl iodides diminish in the order given, that of the sulphide with ethyl iodide is much greater than in the case of ethyl sulphide and *iso*amyl iodide. As the equation, $SR^1R^2 + R^3I = SR^1R^2R^3I$, shows, the speed of the reaction is primarily determined by the mobility of the halogen atom (compare Carrara, A., 1895, ii, 8; Strömholm, A., 1900, i, 325). In conformity with this explanation, *iso*amyl iodide cannot be prepared from the corresponding chloride in the same manner as can benzyl iodide (Späth, A., 1914, i, 1). Double salts of tri*iso*amylsulphonium iodide with zinc, cadmium, and mercuric iodides can, however, easily be prepared by warming mixtures of *iso*amyl iodide and sulphide with the metallic iodide at 100°. *Bistriisoamylsulphine zinci-iodide*, $2S(C_5H_{11})_3I,ZnI_2$, has m. p. 134°; the corresponding *cadmi-iodide*, $2S(C_5H_{11})_3I,CdI_2$, forms yellow needles, m. p. 126—127°, and is decomposed by hot water; the dimercuri-iodide, $3S(C_5H_{11})_3I,2HgI_2$, forms light yellow crystals, m. p. 66—67° to a turbid liquid, becoming clear at a somewhat higher temperature. An indefinite product was obtained from bismuth iodide. Tri*iso*amylsulphonium iodide could not be liberated from its salts, but was probably produced by prolonged action of the iodide on the sulphide in presence of molecular silver. *Diethyl sulphide dimercurichloride*,

$$S(C_2H_5)_2,2HgCl_2,$$

separates from alcohol in colourless crystals, m. p. 127°, which are decomposed by water.

J. K.

Preparation of Acetic Anhydride. FREDERICK PEACOCK LEACH and THE UNITED ALKALI CO., LTD. (Brit. Pat. 137701).—Acetic anhydride is produced by the interaction of anhydrous sodium acetate and carbonyl chloride according to the equation $2CH_3{\cdot}CO_2Na + COCl_2 = (CH_3{\cdot}CO)_2O + CO_2 + 2NaCl$. The reaction is started by suspending sodium acetate in acetic anhydride and adding alternately, with cooling, carbonyl chloride and sodium acetate, keeping the latter in slight excess, until a desired amount of the mixture has been produced. A portion of the liquor is then run off into a still, and the acetic anhydride distilled off in a vacuum, whilst fresh quantities of sodium acetate and carbonyl chloride are added to the mixture remaining in the reaction vessel.

G. F. M.

Preparation of Aliphatic Acids by Catalytic Oxidation of Primary Alcohols. A. MAILHE and F. DE GODON (*Compt. rend.*, 1920, **170**, 517—519).—Primary aliphatic alcohols readily undergo catalytic oxidation in the presence of finely divided copper at 260—270°, giving an appreciable yield of the corresponding acids, but at the same time an important amount of the aldehyde is also formed. In the case of ethyl alcohol, the highest yield obtained was 18·18 grams of acetic acid and 12 c.c. of acetaldehyde from 100 c.c. of alcohol. W. G.

Preparation of Aliphatic Esters. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 315021; from *Chem. Zentr.*, 1919, iv, 1104).—Acetylene is allowed to act on a molar mixture of fatty acid and alcohol in the presence of the mercury salts of mineral acids, preferably at an increased temperature. Thus, acetic acid is agitated with precipitated mercury oxide at 30—40° until complete solution is obtained, after which sulphuric acid (D 1·81) is added drop by drop, which causes the precipitation of mercuric sulphate in a finely divided condition; after addition of ethyl alcohol, the mixture is heated at 70° under reflux, and, with constant agitation, treated with acetylene. Acetaldehyde, which is formed as a by-product, is separated from ethyl acetate by fractional distillation. Ethyl formate is obtained when the acetic acid is replaced by formic acid, whilst methyl propionate is prepared from methyl alcohol and propionic acid. H. W.

Preparation of α-Sulphopropionic Acid. H. J. BACKER and J. V. DUBSKY (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 415—416).—The general methods of Franchimont (A., 1888, 1175) and of Melsens, when applied to the preparation of α-sulphopropionic acid, have the respective advantages of greater purity and better yield of the product. Both of these are conserved by a combination of the two processes, consisting in the addition of crystalline pyrosulphuric acid to propionic anhydride. An average yield of 0·75 mol. of acid per 1 mol. of anhydride is thus obtained. J. K.

Ammonium Tetroxalate, a Product of the Decomposition of *iso*Amyl Nitrite. H. SANDQVIST and E. MOHLIN (*Ber.*, 1920 **53**, [*B*], 171—173).—A crystalline deposit, needles or rods, m. p. 129·5—130·5° (decomp.), deposited on the sides of a bottle containing commercial amyl nitrite which had become extensively decomposed, was found to consist of ammonium tetroxalate. Formation of these crystals in similar circumstances has been observed by Bödtger (A., 1916, i, 2), who, however, overlooked the nitrogen content, and considered them to be methanetetracarboxylic acid. H. W.

***l*-Hexylsuccinic Acid.** HENRY WREN and HENRY BURNS (T. 1920, **117**, 266—268).

The Resolution of Racemic Acids by Optically Active Alcohols. I. The Resolution of r-Tartaric Acid by l-Borneol. HENRY WREN, HOWELL WILLIAMS, and WILLIAM WHALLEY MYDDLETON (T., 1920, **117**, 191—199).

Preparation of Succinyldiacetic Esters. RICHARD WILLSTÄTTER (D.R.-P. 300672; from *Chem. Zentr.*, 1920, ii, 338).—*Neutral or faintly acid solutions of acetonedicarboxylic acid esters* are submitted to electrolysis. The secondary potassium salts of acetonedicarboxylic acid ester are obtained by the action of potassium hydroxide in concentrated aqueous or in alcoholic solution on acetonedicarboxylic esters. The dipotassium salt of ethyl hydrogen acetonedicarboxylate yields, on electrolysis, *ethyl succinyldiacetate*, colourless needles, m. p. 46—47°, which with ammonia or amines yields pyrrole derivatives, for example, 1-*methylpyrrolediacetic ester*, prisms, m. p. 164°. The corresponding methyl derivative of succinyldiacetic acid is formed less smoothly from methyl hydrogen acetonedicarboxylate, and is converted into *dimethyl 1-methylpyrrolediacetate*, needles, m. p. 170—171°. The succinyldiacetic ester constitutes the starting point for the synthetic preparation of derivatives of tropine. H. W.

The Preparation of Glyoxal by the Action of Ozone on Acetylene. A. WOHL and K. BRÄUNIG (*Chem. Zeit.*, 1920, **44**, 157).—*It is well known that ozone and acetylene interact* with explosive violence. It has now been found that when the gases are suitably diluted and contain a certain amount of moisture, interaction proceeds smoothly, with formation of a mixture of glyoxal and formic acid. The products are obtained as an aqueous solution by spraying water into the reaction vessel. The solution contains 1·5 to 2·0% of glyoxal. A certain amount of nitric acid is formed at the same time, and this must be neutralised before the solution is evaporated, to avoid decomposition of the glyoxal. The latter can be isolated by known methods, for example, as its aniline derivative, or can be directly converted into glycollic acid or ethylene glycol. *The aniline derivative, the anilide of anilinoacetic* acid, can be used for the preparation of indigotin. E. H. R.

Preparation of Monobromoacetone. J. D. RIEDEL (D.R.-P. 298944; from *Chem. Zentr.*, 1920, ii, 337).—Solutions of bromine in bromide liquors are added to hot solutions of acetone containing bromoacetone in bromide liquors; the latter are obtained by neutralising the aqueous solutions from previous preparations. Monobromoacetone is thus obtained in good yield and in an *immediately pure condition.* H. W.

Preparation of Monobromo-ketones. J. D. RIEDEL (D.R.-P. 298953, additional to D.R.-P. 298944; from *Chem. Zentr.*, 1920, ii, 337. Compare preceding abstract).—Solutions of bromine in bromide liquors are added at an elevated temperature to solutions of the homologues of acetone (containing the bromo-ketone) or to a mixture of ketones and bromide liquors; the neutralised aqueous solutions from previous preparations are utilised as bromide liquors.

The instance of bromomethyl ethyl ketone, transparent, yellow liquid, is cited in particular. H. W.

A New Hydrazone of some Monosaccharides (*m*-Tolylhydrazones of *l*-Arabinose, Rhamnose, Fucose, *d*-Galactose, and *d*-Mannose). A. W. VAN DER HAAR (*Rec. trav. chim.*, 1920, **39**, 191—193).—*m*-Tolylhydrazine gives the following hydrazones: l-*arabinose*-m-*tolylhydrazone*, prismatic needles, m. p. 156—157°; *rhamnose*-m-*tolylhydrazone*, m. p. 134°; *fucose*-m-*tolylhydrazone*, microscopic needles, m. p. 165°; d-*mannose*-m-*tolylhydrazone*, amorphous; d-*galactose*-m-*tolylhydrazone*, needles, m. p. 154°. Xylose and *d*-fructose did not give such hydrazones, and the one from dextrose could not be obtained sufficiently pure. W. G.

Oxidation of Sugars by Mercuric Acetate in the Presence of Ammonia. T. INGVALDSEN and L. BAUMAN (*J. Biol. Chem.*, 1920, **41**, 147—148).—Ammonium gluconate and ammonium galactonate may be obtained in 50% yield by the action of mercuric acetate on dextrose or galactose in the presence of ammonia. Mannose and lactose are also oxidised by this method, but the ammonium salts of the acids formed have not been isolated in crystalline form. J. C. D.

The Heptoses from Gulose and some of their Derivatives. F. B. LA FORGE (*J. Biol. Chem.*, 1920, **41**, 251—256).—Gulose was converted into a mixture of α- and β-guloheptonic acids by the cyanide synthesis. A mixture of the barium salts yielded on crystallisation rosettes of plates of the barium salt of α-guloheptonic acid, $C_{14}H_{26}O_{16}Ba$.

α-*d*-Guloheptonic acid was a colourless syrup, which did not crystallise. It yielded a crystalline *phenylhydrazide*, long, white needles, m. p. 191—192° (uncorr.), $[\alpha]_D^{20}$ −15·38°.

α-d-*Guloheptose*, $C_7H_{14}O_7$, obtained by reduction with sodium amalgam, forms rosettes of long needles, m. p. 185—187° (uncorr.), $[\alpha]_D^{20}$ −65·65°.

α-Guloheptitol, $C_7H_{16}O_7$, rosettes of hard prisms, m. p. 138—141° (uncorr.). No rotation was shown by an approximately 5% solution in water. 1·0624 Grams in 25 c.c. of saturated borax solution gave in a 4-dcm. tube α_D +0·68°.

β-Guloheptonic acid and *β-guloheptose* were obtained from the mother liquors of the barium salt of α-guloheptonic acid. On reduction of the syrupy β-guloheptose, another syrup was obtained, which, as it did not crystallise, was converted into *benzylidene-β-guloheptitol*, m. p. 260° (decomp.).

β-Guloheptitol, $C_7H_{16}O_7$, has m. p. 128—129° (uncorr.). 0·3175 Gram in 5 c.c. of saturated borax solution showed no appreciable rotation in a 1-dcm. tube. J. C. D.

The Constitution of the Disaccharides. IV. The Structure of the Fructose Residue in Sucrose. WALTER NORMAN HAWORTH (T., 1920, **117**, 199—208).

Biochemical Synthesis of a Mannobiose. EM. BOURQUELOT and H. HERISSEY (*J. Pharm. Chim.*, 1920, [vii], **21**, 81—85).—The enzyme seminase (A., 1900, i, 320) obtained from lucerne seeds, when kept for ten months in concentrated mannose solution containing a small quantity of toluene, converted the mannose, in part, into a sugar having a higher optical rotation. This sugar was isolated in an impure state, and appeared to be a mannobiose.
W. P. S.

Determination of the Value of Different Acids for the Liquefaction of Starch. P. BETTINGER (*Bull. Assoc. Chim. Sucr.*, 1919, **37**, 126—131).—The relative activities of hydrochloric, sulphuric, and certain organic acids in producing liquefaction of the starch in ground cereals, under similar conditions of heating, are accounted for by the different degrees of ionisation of the acids. [See, further, *J. Soc. Chem. Ind.*, 1920, 244A.] J. H. L.

Action of Saliva Ash on Starch Solution. FR. N. SCHULZ (*Fermentforsch.*, 1919, **3**, 72—74; from *Chem. Zentr.*, 1920, i, 8—9).—In repeating Biedermann's experiments (this vol., i, 15) with saliva ash, the author has encountered the same difficulties as Wohlgemuth and Sallinger. Since the ash was strongly alkaline in reaction, whilst Biedermann describes the use of a neutral or faintly acid ash, and, on the other hand, the dependence of diastatic processes on the reaction is well known, the ash was made very faintly acid with hydrochloric acid. Reaction was immediately observed, which could be stopped by addition of an excess of the acid. The time of action varied between twenty minutes and several (generally four to six) hours. Optimum action probably depends on the absolute quantity of ash and a definite degree of acidity. Urine ash, when kept faintly acidic, invariably gives a positive result. H. W.

Autolysis of Starch. Reply to Wohlgemuth and Sallinger. W. BIEDERMANN (*Fermentforsch.*, 1919, **3**, 70—71; from *Chem. Zentr.*, 1920, i, 9. Compare this vol., i, 15).—The discordant results obtained by Wohlgemuth (A., 1919, i, 361) and Sallinger (this vol., i, 15) are explained by the different reaction of the saliva ash in the various instances. The ash used by the author was neutral or very faintly acidic; it now appears that this behaviour is exceptional, and that the hydrolysis of starch by saliva ash is dependent on the reaction of the latter, as is to be expected from the known influence of alkali on amylase action (compare Schulz, preceding abstract). H. W.

Lignin. II. Fusion of the Lignosulphonic Acids with Potassium Hydroxide. MAX HÖNIG and WALTER FUCHS (*Monatsh.*, 1919, **40**, 341—349).—The removal of the sulphonic groups from the barium salts previously described (A., 1918, i, 375) by fusion with potassium hydroxide is only complete at 250—300°. In each case, protocatechuic acid is the sole product (compare Melander,

A., 1919, i, 473) obtained after solution of the fused mass in water, acidification, filtration from insoluble matter (amounting to about one-third of the purely organic portion of the original material), and extraction with ether, the quantity obtained corresponding with 13—19% of the organic portion of the original material. In addition, a small quantity of material is not removed from the aqueous solution by ether. The lignosulphonic acids are therefore complicated aromatic sulphonic acids containing the carbon skeleton of protocatechuic acid. J. K.

Preparation of Methylamine from Ammonium Methyl Sulphate. WILLIAM SMITH DENHAM and LIONEL FREDERICK KNAPP (T., 1920, **117**, 236—247).

Double Salts of Cerium Tetrachloride. F. DI STEFANO (*Annali Chim. Appl.*, 1919, **12**, 130—136).—Owing to the instability of quadrivalent cerium, the tetrachloride of that metal has not been isolated, but Koppel (A., 1899, ii, 98) prepared stable double salts of cerium tetrachloride with pyridine, quinoline, and triethylamine, which he concluded to be derivatives of a hydrochloroceric acid, H_2CeCl_6. Various new double salts of this acid are now described. The *tetramethylammonium* salt,

$$CeCl_4,2N(CH_3)_4Cl,$$

was prepared by adding a concentrated solution of tetramethylammonium chloride in methyl alcohol to a solution of ceric chloride in the same solvent, and washing the resulting yellow, crystalline precipitate first with methyl alcohol saturated with hydrogen chloride, and then with ether. It is stable in absolutely dry air, but completely decomposed on exposure to moist air, and when dissolved in water rapidly liberates chlorine. The *tetraethylammonium* salt, $CeCl_4,2N(C_2H_5)_4Cl$, is obtained in an analogous manner. It is much more stable than the preceding compound, and is only slowly decomposed when dissolved in water. It liberates iodine from potassium iodide (ratio of Ce to active Cl = 1 : 0·99). The *caffeine* salt, $CeCl_4(C_8H_{10}O_2N_4,HCl)_2$, forms reddish-orange, silky crystals which are quite stable in dry air, and only decompose slowly in moist air (ratio of Ce to active Cl = 1 : 1·06). Theobromine hydrochloride gave a yellow, crystalline powder with cerium tetrachloride, the exact composition of which could not be determined owing to the presence of the excess of alkaloid hydrochloride, but was probably $CeCl_4,2(C_7H_8O_2N_4,HCl)$. The *quinine* salt, $CeCl_4,2(C_{20}H_{24}O_2N_2,2HCl)$, was obtained in large, reddish-orange crystals, in which the ratio of cerium to active chlorine was 1 : 1. C. A. M.

A New Method for the Preparation of Hexamethylenetetramine. WALTHER HERZOG (*Zeitsch. angew. Chem.*, 1920, **33**, 48).—If commercial ammonium carbonate is treated with 40% formaldehyde solution, it readily dissolves, even without application of heat, with brisk evolution of carbon dioxide and formation of hexamethylenetetramine. The solution is evaporated to dryness on a

water-bath under reduced pressure, and the residue is either sublimed in a vacuum or recrystallised from absolute alcohol. The amount of ammonium carbonate should be about 10% in excess of the theoretical quantity. A yield of about 66% is obtained.

W. J. W.

Solubility of Hexamethylenetetramine. F. UTZ (*Süddeutsch. Apoth. Zeit.*, 1919, **59**, 832; from *Chem. Zentr.*, 1920, i, 170).—1·67 Grams of hexamethylenetetramine dissolve in one part of water at the ordinary temperature (D 1·0985); larger quantities dissolve in hot water and separate on cooling the solution. At the ordinary temperature, 100 c.c. of the solvents dissolve the following amounts of hexamethylenetetramine, expressed in grams: ethyl ether, 0·06 (on warming, 0·38); trichloroethylene, 0·11; xylene, 0·14; carbon disulphide, 0·17; benzene, 0·23; tetrachloroethane, 0·50; acetone, 0·65; carbon tetrachloride, 0·85; amyl alcohol, 1·84; absolute alcohol, 2·89; 90% alcohol, 5·58 (large quantities dissolved in the hot solvent separate from the cooled solution until the latter contains 6·4 grams); methyl alcohol, 7·25 (in warm solution, 11·93). Chloroform is the best solvent, the cold solution containing 13·40 and the hot solution 14·84 grams; the bulk of the dissolved substance can be precipitated from its solution in chloroform by addition of ether. Hexamethylenetetramine is insoluble in light petroleum. When obtained from solution and dried in the steam-oven, hexamethylenetetramine is somewhat volatile with the vapour of the solvent, 18·38% of it being removed in forty hours. Determination of the refraction is best effected in aqueous methyl-alcoholic solution.

H. W.

Metallic Compounds of Glycine and Asparagine. II. A. BERNARDI (*Gazzetta*, 1919, **49**, ii, 318—325. Compare A., 1914, i, 1167).—The double *compound* of mercury aminoacetate (compare Ley and Kissel, A., 1899, ii, 485) and mercuric chloride,

$(NH_2\cdot CH_2\cdot CO_2)_2Hg,HgCl_2,H_2O$,

prepared from glycine and mercuric chloride in dilute alcohol at 50—60°, forms a white, infusible precipitate, which gradually loses its water of crystallisation in the air.

The double *compound* of mercury asparagine and mercuric sulphate, $[NH_2\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CO_2]_2Hg,HgSO_4$, forms a white, flocculent precipitate and decomposes, without melting, at a high temperature; it is rapidly decomposed in the hot by concentrated potassium hydroxide solution and by ammonia solution, with precipitation of mercury in the former case and of mercuriammonium sulphate in the latter.

The *chromium* compound of asparagine,

$[NH_2\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CO_2]_3Cr,H_2O$,

prepared from asparagine and chromic acetate, crystallises in tufts of amaranth-red needles, forms an alkaline aqueous solution, and decomposes at about 200°. The *nickel* compound of asparagine, $[NH_2\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CO_2]_2Ni,2H_2O$, prepared from asparagine and nickel hydroxide, crystallises in blue, rectangular plates, has

an alkaline reaction in boiling aqueous solution, and decomposes at above 200°. The *cobalt* compound,

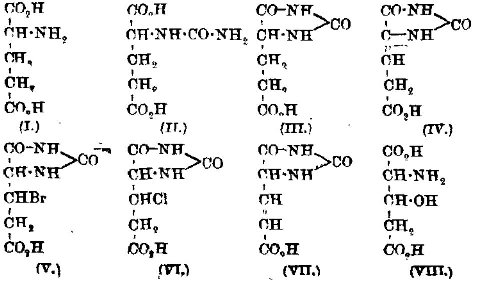
$$[NH_2\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CO_2]_2Co,2H_2O,$$

prepared from asparagine and cobalt hydroxide, crystallises in amaranth-red mamillary masses, shows an alkaline reaction in boiling aqueous solution, and decomposes at above 200°.

T. H. P.

Amino-acids. II. Hydroxyglutamic Acid. HENRY DRYSDALE DAKIN (*Biochem. J.*, 1919, **13**, 398—429).—The author has described previously the isolation of β-hydroxyglutamic acid from the products of hydrolysis of caseinogen (A., 1919, i, 150).

Attempts to synthesise this acid by brominating the acetyl derivative of β-hydroxyglutaric anhydride, and then acting on the bromo-compound with ammonia or by reducing ethyl α-oximinoacetonedicarboxylate, were unsuccessful. Small traces of a substance closely resembling the desired amino-acid were obtained, after some difficulty, by reducing with sodium amalgam the condensation product of orthoformic ester and ethyl oximinoacetonedicarboxylate, and a similar result was obtained by the application of Strecker's method to malic semialdehyde. More satisfactory results were obtained with glutamic acid (I), which was converted into α-carbamidoglutaric acid (II) by the action of potassium cyanate, and hydantoinpropionic acid (III) was obtained from the carbamido-acid by the action of hydrochloric acid. The action of bromine on hydantoinpropionic acid in concentrated solutions in glacial acetic acid gave two products. One would appear to be *hydantoin-β-bromopropionic acid* (V) and the other *hydantoin-βγ-propenylic* acid. If the action of bromine is carried out in presence of fuming hydrochloric acid, hydantoin-β-chloropropionic acid (VI) is obtained. The conversion of hydantoin-β-bromopropionic acid into the desired hydroxyglutamic acid was not accomplished with ease. On boiling with water, an unsaturated acid (VII) is obtained, which, on prolonged treatment with hot barium



(I.) (II.) (III.) (IV.) (V.) (VI.) (VII.) (VIII.)

hydroxide solution, is converted into β-hydroxyglutamic acid (VIII). Calculated on the original glutamic acid, the yield is about 2%.

Sufficiently large amounts of the new amino-acid were not obtained to permit of a detailed study, but its properties are all similar to those of the naturally occurring acid isolated from caseinogen. It gives a cherry-red colour with diazobenzene-sulphonic acid in the presence of sodium hydroxide, which becomes intensely deep on warming.

Other methods of synthesis were attempted, but were not found practicable. Such were bromination of benzoylglutamic acid, with the hope of obtaining benzoylaminoglutaconic acid by removal of hydrobromic acid; reduction of *o*-toluidineazoacetonedicarboxylic ester, and of various hydrazine derivatives of that ester; condensation of oxymethylenehippuric ester with malonic ester; condensation of dichloroacetal with malonic ester, followed by reactions analogous to Leuch's synthesis of serine; reduction of oximino-glutaconic ester and of ethyl hydroxy*iso*oxazoledicarboxylate.

The following compounds are described: *Hydantoin-β-bromopropionic acid*, $C_8H_7O_4N_2Br$ (V), white cubes and rhombic prisms, m. p. 228—230° (decomp.). *Hydantoin-βγ-propenylic acid*, $C_8H_6O_4N_2$ (IV), sulphur-yellow, hexagonal prisms, m. p. 222—223°, solid sublimate being obtained. *Hydantoin-β-chloropropionic acid*, $C_8H_7O_4N_2Cl$, rectangular plates. *Hydantoinacrylic acid* (VII), $C_6H_6O_4N_2$, rosettes of sulphur-yellow needles, m. p. 256—258° (decomp.). β-Hydroxyglutamic acid (VIII), $C_5H_9O_5N$, passes, on heating, into hydroxypyrrolidonecarboxylic acid. Copper salt, very soluble in water, insoluble in alcohol. *Strychnine* salt, $C_{26}H_{31}O_7N_3$, rosettes of needles. Malic semialdehyde, or β-hydroxy-γ-aldehydobutyric acid, $C_4H_6O_4$, did not crystallise; its *semicarbazone*, $C_5H_9O_4N_3$, forms prisms, m. p. 211°: the *p-nitrophenylosazone*,

$$C_{16}H_{14}O_6N_6,$$

m. p. 297—299° (corr.). This compound was identical with the *p*-nitrophenylosazone prepared from the aldehyde produced on the oxidation of the natural hydroxyglutamic acid. β-Hydroxy-γγ-diethoxybutyric acid, $C_8H_{16}O_5$, clear oil, b. p. 120°/5 mm., possesses a sour odour. The *nitrophenylosazone* of the related tartronic semialdehyde, $C_{15}H_{12}O_6N_6$, m. p. 310° (corr.), forms rosettes of fine needles.

β-Hydroxyglutamic acid in 4% solution in water has $[\alpha]_D^{20}$ about +0·8°, but a 2% solution in hydrochloric acid has $[\alpha]_D^{20}$ +16·3°. The rotation of the potassium salt is practically undetectable, but the addition of uranium nitrate renders it strongly lævorotatory. *Strychnine d-β-hydroxyglutamate*, prismatic needles, m. p. 245°, $[\alpha]_D^{20}$ −26·3°. *Brucine d-β-hydroxyglutamate*, $C_{28}H_{35}O_9N_3$, needles, decomp. about 200°, $[\alpha]_D^{20}$ −25·0°. *Strychnine* d-*glutamate*, $C_{26}H_{31}O_6N_3$, glistening prisms, m. p. 225—230°, decomp. above 200°, $[\alpha]_D^{20}$ −25·5°. *Brucine* d-*glutamate*, $C_{28}H_{35}O_8N_3,5·5H_2O$, m. p. 101°, anhydrous salt, m. p. 240°, stout, prismatic needles with satin lustre, $[\alpha]_D^{20}$ −23°. *Strychnine* l-*aspartate*, $C_{25}H_{29}O_6N_3$,

fine needles, m. p. 252—255°, $[\alpha]_D^{20}$ −28·3°. *Brucine* 1-*aspartate*, $C_{27}H_{33}O_8N_3,5H_2O$, fine needles, m. p. 100°; anhydrous salt, m. p. 200°, $[\alpha]_D^{20}$ −28·4°. *Strychnine* 1-*a-pyrrolidonecarboxylate*, fan-shaped masses of fine needles, m. p. 245°, $[\alpha]_D^{20}$ −26·7°. *Brucine* 1-*a-pyrrolidonecarboxylate*, well-formed prisms, m. p. 180—185°, decomp. above 140°, $[\alpha]_D^{20}$ −31·5°.

β-Hydroxyglutamic acid was isolated to the extent of 2·4% from gliadin and 1·8% from glutein. When administered to the phloridzinised dog, β-hydroxyglutamic acid yields 55—60% of its weight as dextrose, apparently three of its five carbon atoms being concerned in sugar formation. J. C. D.

Preparation of Derivatives of Bromoacylised Carbamide Compounds. FARBENFABRIKEN VORM. F. BAYER & Co. (Brit. Pat. 132795).—On treating bromoacylised carbamide compounds with acylising agents in presence of condensing agents, such as zinc chloride or sulphuric acid, acyl compounds are obtained which have a rapid but lasting sedative and soporific action. Examples are given of the preparation of *acetylbromo-a-ethylbutyrylcarbamide*, m. p. 108—109°, from bromo-a-ethylbutyrylcarbamide (474 parts), acetic anhydride (1000 parts), and zinc chloride (75 parts), the mixture being heated for one hour at 60° and then poured into iced water (3000 parts); of *acetylbromoisovalerylcarbamide*, m. p. 108—109°, from bromo*iso*valerylcarbamide and acetic anhydride; of *propionylbromo-a-ethylbutyrylcarbamide*, m. p. 103°; and of *benzoylbromo-a-ethylbutyrylcarbamide*, m. p. 139—140°, sulphuric acid being employed as condensing agent in each of the last three examples. G. F. M.

Compounds of Univalent Nickel. III. I. BELLUCCI (*Gazzetta*, 1919, **49**, ii, 285—293).—Repetition of the work of Moore (compare A., 1894, i, 102; 1895, ii, 168) yields the following results. When treated in the hot with ammonium chloride solution, ordinary potassium nickelocyanide reacts only in virtue of the potassium cyanide it contains, the nickelous cyanide remaining unchanged: $K_2Ni(CN)_4 + 2NH_4Cl = Ni(CN)_2 + 2KCl + 2NH_4CN$. With the red nickelocyanide (compare A., 1919, i, 526), under similar conditions, two distinct reactions take place: (1) An oxidation, which depends on the marked tendency of the red salt to undergo conversion into the ordinary yellow nickelocyanide, and may follow one of the two schemes, $4K_2Ni(CN)_3 \xrightarrow{2O} 3K_2Ni(CN)_4 + K_2O + NiO$ and

$$4K_2Ni(CN)_3 \xrightarrow{O} 3K_2Ni(CN)_4 + K_2O + Ni.$$

If the reaction is carried out in an inert medium or with the intervention solely of the combined oxygen of the water, as in Moore's experiments, the process of oxidation should proceed mainly according to the second of these two schemes. (2) Precipitation of nickelous cyanide as a result of the action of the ammonium chloride on the yellow potassium nickelocyanide formed in reaction (1). The oxidation (1) proceeds very rapidly, since the

ammonium chloride undergoes gradual hydrolysis and loss of ammonia, the hydrochloric acid thus liberated in the solution uniting with the potassium oxide formed during the oxidation. These conclusions are completely verified by the experimental results.

Moore's supposed suboxide, $Ni_3O,2H_2O$, consists of a mixture of pulverulent metallic nickel with hydrated nickelous oxide, NiO,Aq.

T. H. P.

Preparation of the Tri- and Tetra-carboxylic Esters of Hydrazine and of Ethyl *as*-Hydrazinedicarboxylate. OTTO DIELS and ERICH BORGWARDT (*Ber.*, 1920, **53**, [*B*], 150—158).—*Dicarboxyethylnitroamide* [*ethyl nitroiminodicarboxylate*],

$NO_2 \cdot N(CO_2Et)_2$,

b. p. 115—117°/14 mm., was prepared by the action of ethyl chloroformate on the potassium salt of nitrourethane in boiling toluene solution; attempts to reduce it to ethyl *as*-hydrazinedicarboxylate were unsuccessful, since ethyl iminodicarboxylate was formed with zinc dust in alcoholic solution or with sodium amalgam in moist ether, whilst the action of stannous chloride in ethereal solution in the presence of hydrogen chloride yielded the iminodicarboxylic ester and hydroxylamine hydrochloride. Better results were obtained by acting on the potassium derivative of ethyl benzylidenehydrazinecarboxylate with ethyl chloroformate, whereby *ethyl benzylidenehydrazinedicarboxylate*, $CHPh\colon N \cdot N(CO_2Et)_2$, prisms, m. p. 38—39° after softening at 37°, was obtained, which, when treated with phenylhydrazine in boiling aqueous-alcoholic solution, gave benzaldehydephenylhydrazone and *ethyl as-hydrazinedicarboxylate*, silvery prisms, m. p. 29—30°, b. p. 138—139°/12 mm. (the *hydrochloride*, m. p. 83·5° [? aq.], m. p. 107—108° [after desiccation over phosphoric oxide at 35°], was analysed). The ester was decomposed by distillation under ordinary pressure, yielding ethyl *s*-hydrazinedicarboxylate and a reddish-brown resin; it was converted by *o*-nitrobenzaldehyde into *ethyl o-nitrobenzylidenehydrazinedicarboxylate*, pale yellow crystals, m. p. 26—27°.

Ethyl *as*-hydrazinedicarboxylate was treated with ethyl chloroformate in dry ethereal solution, whereby a mixture of ethyl *as*-hydrazinedicarboxylate and ethyl hydrazinetricarboxylate was formed; the latter was transformed by the successive action of potassium and ethyl chloroformate in toluene solution into *ethyl hydrazinetetracarboxylate*, colourless, highly refractive, viscous oil, b. p. 145—146°/0·65 mm.

The preparation of *ethyl hydrazinetricarboxylate*, colourless, highly refractive oil, b. p. 184—186°/9 mm. (slight decomp.), was effected by the successive action of sodium and ethyl chloroformate on an ethereal solution of ethyl hydrazinecarboxylate (ethyl *s*-hydrazinedicarboxylate, long needles, m. p. 131°, was simultaneously formed), or by the interaction of ethyl chloroformate and ethyl *as*-hydrazinedicarboxylate. Investigation of the ester is not yet completed, but it has been shown that one ester group is readily

eliminated; thus, aqueous potassium hydroxide solution was found to convert it into ethyl *s*-hydrazinedicarboxylate and potassium carbonate,

$$CO_2Et\cdot NH\cdot N(CO_2Et)_2 + H_2O = CO_2 + EtOH + (NH\cdot CO_2Et)_2,$$

whilst propylamine transformed it into a mixture of ethyl *s*-hydrazinedicarboxylate and *dipropylurethane*, colourless, pleasant-smelling liquid, b. p. 83°/10 mm. H. W.

Reduction of Aromatic Nitro-compounds by means of Platinum and Hydrogen. G. Cusmano (*Annali Chim. Appl.*, 1919, **12**, 123—130).—Aromatic nitro-compounds in ethereal solution are rapidly reduced to amines when shaken with platinum-black in an atmosphere of hydrogen. A gradual reduction through nitroso-compounds and hydroxylamines is thus effected in the case of nitroterpenes, whereas in the case of aromatic compounds only a mixture of amines and unaltered nitro-compounds is obtained. The reduction has been found to proceed as shown in the following equations in the case of *p*-nitrophenol, *p*-nitroanisole, *p*-nitrotoluene, *o*-nitrotoluene, and *m*-nitroaniline, although sufficient hydrogen was supplied for the formation of the intermediate nitroso-compounds or β-hydroxylamines:

$$3R\cdot NO_2 + 3H_2 = 2R\cdot NO_2 + R\cdot NH_2 + 2H_2O,$$
$$3R\cdot NO_2 + 6H_2 = R\cdot NO_2 + 2R\cdot NH_2 + 4H_2O.$$

The reduction of certain nitroso-compounds into hydroxylamines follows a similar course. The above-mentioned reactions do not agree with those obtained by reduction with ordinary chemical or electrochemical reagents, which proceed as follows: $R\cdot NO_2 \longrightarrow R\cdot NO \longrightarrow R\cdot NH_2O \longrightarrow R\cdot NH_2$. The nitroso-compounds are always produced in small quantity, but under favourable conditions good yields of the β-hydroxylamines are obtained. β-Hydroxylamines offer more resistance than nitro-compounds to the action of ordinary reducing agents, but are reduced more readily than nitro-compounds by hydrogen and platinum-black. The velocity of the reduction of a β-hydroxylamine depends also on that of its transformation into the tautomeric form containing nitric nitrogen, $R\cdot NH\cdot OH \rightleftharpoons O{:}NH_2R$. This transformation may become very rapid when the radicles in the hydroxylamine have no influence on either form, but in acid media, or in the presence of negative radicles tending to stabilise the first (aminic) form, there may be retardation of the reduction, so that the velocity of reduction, from being equal or superior to that of a nitro-compound, may become less than that of the latter. Preliminary experiments have shown that in the case of a mixture of *p*-nitrotoluene and azoxybenzene, the former is preferentially reduced. C. A. M.

Remarkable Instance of Isomerism in the Naphthalene Series. Hartwig Franzen and Fritz Helwert (*Ber.*, 1920, **53**, [*B*], 319—322).—For investigation of the replaceability of the chlorine atoms in chloronitronaphthalenes, the authors have required 1-chloro-4-nitronaphthalene, pale yellow crystals, m. p.

85°, which they have prepared with difficulty in accordance with Atterberg's directions, and have confirmed his results. As, however, the yields are bad, they have also prepared it from 4-nitro-α-naphthamine by Sandmeyer's reaction as modified by Ullmann; in general, the product obtained in this manner was identical with that prepared by nitration of α-chloronaphthalene, but on one occasion, without apparent variation in conditions, the *substance* which was isolated formed yellowish-green crystals, m. p. 60—61°, and gave analytical results agreeing with those required for 1-chloro-4-nitronaphthalene. This is not a case of physical isomerism, since it is not possible to convert the more fusible into the less fusible substance, and since also the two substances yield different *piperidino*-derivatives, yellowish-brown needles, m. p. 70—71°, and yellowish-brown needles, m. p. 63—64°, respectively, whilst also the rates of reaction with piperidine are very different in the two cases. As there appears to be no possible doubt as to the purity and uniformity of the starting materials, an instance of isomerism which is inexplicable by the aid of the generally accepted formula of naphthalene seems to be presented. Unfortunately, it has not been found possible up to the present to repeat the preparation of the isomeride, m. p. 60—61°. H. W.

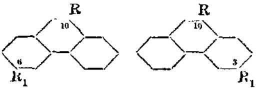
Synthesis of 3:10-Dichlorophenanthrene. PAUL NYLÉN (*Ber.*, 1920, **53**, [*B*], 158—167).—The experiments were undertaken with the object of elucidating the constitution of some of the dichlorophenanthrenes obtained by Sandqvist and Hagelin (A., 1919, i, 11); the substance described by these authors as 11-10:3(6)-dichlorophenanthrene is found to be identical with 3:10-dichlorophenanthrene.

α-p-*Chlorophenyl-o-nitrocinnamic acid*, $\begin{matrix}NO_2\cdot C_6H_4\cdot C\cdot H \\ C_6H_4Cl\ C\cdot CO_2H\end{matrix}$, is best obtained by heating potassium *p*-chlorophenylacetate with o-nitrobenzaldehyde and acetic anhydride, filtration from acid potassium acetate, and dilution of the filtrate with a regulated amount of water, whereby the acid is precipitated as pale yellow cubes, m. p. 190·2—190·7° (corr.). (The *ammonium* salt, yellow, lustrous needles, *barium* salt, yellow cubes, and *calcium* salt, prisms, are described.) Further dilution of the filtrates mentioned above yields a further precipitate, from which allo-*α*-p-*chlorophenyl-o-nitrocinnamic acid*, $\begin{matrix}NO_2\cdot C_6H_4\cdot C\cdot H \\ CO_2H\cdot C\cdot C_6H_4Cl\end{matrix}$, m. p. 148·5—150° (corr.), is isolated. The substance is characterised as the *allo*-acid by its lower melting point, the greater solubility of its salts (the *ammonium* salt is described), its non-isomerisation by iodine, its sensibility to the action of light, and the formation of a *compound* with aniline, yellow needles, m. p. 124°.

α-p-*Chlorophenyl-o-aminocinnamic acid* is formed in a yellow and a colourless modification, both of which have m. p. 224°, by the reduction of the nitro-acid with ferrous sulphate and ammonia (the *hydrochloride*, *sulphate*, and *ammonium*, *calcium*, and *barium* salts are described), and is transformed by acetic anhydride in the

presence of concentrated sulphuric acid into *β-p-chlorophenylcarbostyril*, long, colourless needles, m. p. 258·5—259·5° (corr.). Diazotisation converts the amino-acid into *a-p-chlorophenyl-o-diazocinnamic acid*, yellow flocks, which are stable at the ordinary temperature but explode at 101°, from which *3-chlorophenanthrene-10-carboxylic acid*, colourless needles, m. p. 301·5—302·5°, is best obtained by the use of copper powder (the *calcium, barium, copper, iron*, and *silver* salts are described). Distillation under diminished pressure effects the partial conversion of the acid into 3-chlorophenanthrene, m. p. 80—81°, whilst oxidation with chromic acid converts it into 3-chlorophenanthraquinone, yellow needles, m. p. 264·5—265° (corr.) (compare Sandqvist and Hagelin, *loc. cit.*). *Ethyl 3-chlorophenanthrene-10-carboxylate* crystallises in long, colourless, shining needles, m. p. 94·5—95°, and is converted by hydrazine hydrate into the corresponding *hydrazide*, m. p. about 270°, which, with benzaldehyde and acetone, respectively, yields the corresponding *benzylidene* derivative, colourless, prismatic needles, m. p. 248—249° (corr.), and iso*propylidene* derivative, long, colourless needles, m. p. 243—245° (corr.). Diazotisation of the hydrazide is best effected by nitrous fumes, and yields the corresponding *azide*, m. p. about 96° (decomp.). The latter is converted by boiling absolute alcohol into *3-chloro-10-phenanthrylurethane*, $C_{14}H_8Cl\cdot NH\cdot CO_2Et$, colourless, slender needles, m. p. 197·5° (corr.) after previous softening, which, on treatment with boiling concentrated hydrochloric acid, yields *3-chloro-10-aminophenanthrene*, pale yellow prisms and needles, m. p. 141·2—142·2° (corr.). [The *hydrochloride*, m. p. about 230°, and the *monobenzoyl* derivative, colourless, silky needles, m. p. 257·5° (corr.), are described.] Diazotisation of the amine and treatment of the yellow *diazonium* compound with cuprous chloride leads to the formation of 3:10-dichlorophenanthrene, colourless, slender needles, m. p. 117—117·5° (corr.), in rather poor yield. H. W.

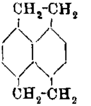
Constitution of Two Series of Doubly Substituted Phenanthrene Derivatives. 3:9-Dibromophenanthrene. HÅKAN SANDQVIST (*Ber.*, 1920, **53**, [*B*], 168—171).—In previous communications, several disubstituted phenanthrenes have been described in which one substituent is present in the bridge (say in position 10), the other in position 3 or 6; two genetic series have thus been prepared, which have been provisionally designated I and II. The allocation of the annexed formulæ to the members of the two series is rendered difficult, since the atom in the bridge is affected by oxidation, and the frequently assumed aliphatic character of the linking in the bridge is not such as to allow the ready replacement of the substituting atom by other groups. The synthesis of 3:10-dichlorophenanthrene by Nylén (preceding



abstract) has, however, shown that this substance is identical with II-10 : 3(6)-dichlorophenanthrene obtained by Sandqvist and Hagelin (A., 1919, i, 11), so that all derivatives belonging to the I series are 10 : 6(=9 : 3)-compounds, whilst those belonging to the II series are 10 : 3(=9 : 6)-substances.

Potassium 10-bromophenanthrene-6-sulphonate is converted by phosphorus pentabromide into *10-bromophenanthrene-6-sulphonyl bromide*, yellow prisms, m. p. 202—203° (slight decomp.), which is converted by further action of the same reagent into *3 : 9-dibromophenanthrene*, pale yellow needles and prisms, m. p. 143—143·5°. Chromic acid converts the latter into 3-bromophenanthraquinone. H. W.

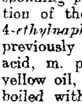
The Acenaphthene Series. I. FRITZ MAYER and WALDEMAR KAUFMANN (*Ber.*, 1920, **53**, [*B*], 289—298).—The experiments were undertaken with the twofold object of preparing technically valuable derivatives of acenaphthene and of synthesising *aceacenaphthene* (annexed formula); the latter purpose has not been effected up to the present.



Dibromoacenaphthene tetrabromide, colourless crystals, m. p. 179—180°, is prepared by the addition of a solution of bromine in chloroform to a boiling solution of acenaphthene in the same solvent; it is converted by boiling concentrated alcoholic potassium hydroxide solution into *tetrabromoacenaphthene*, orange crystals, m. p. 180—181°.

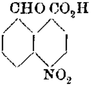
5-Ethylacenaphthene is obtained as an oil, b. p. ca. 166°/20 mm., 310°/atmos. pressure, by the action of ethyl bromide on acenaphthene in the presence of aluminium chloride. The corresponding *picrate* forms red crystals, m. p. 95—96°. The constitution of the hydrocarbon is deduced from its oxidation through *4-ethylnaphthalene-1 : 8-dicarboxylic anhydride*, m. p. 180°, to the previously described anhydride of naphthalene-1 : 4 : 8-tricarboxylic acid, m. p. 248°. Bromination of 5-ethylacenaphthene gives a yellow oil, b. p. above 170°/vac., which remains unchanged when boiled with an excess of alcoholic potassium hydroxide solution. Distillation of 5-ethylacenaphthene with zinc dust yields acenaphthylene.

5-Chloroacetylacenaphthene, m. p. 104°, is prepared by the action of chloroacetyl chloride on the hydrocarbon in the presence of aluminium chloride. Nitration of 5-acetylacenaphthene by nitric acid (D 1·39) in the presence of glacial acetic acid gives *3-nitro-5-acetylacenaphthene*, m. p. 204°. Pyridino-4 : 5-acenaphthene has m. p. 60—61°, whereas Zinke and Raith (this vol., i, 89) give 67°.



5-Nitroacenaphthene-1 : 2-quinone (annexed formula), slender, yellow needles, m. p. 199°, is prepared by the nitration of acenaphthenequinone by concentrated sulphuric acid and nitric acid (D 1·51). (The *mono-* and *di-phenylhydrazones* form dark reddish-brown needles, m. p.

186°, and darker crystals, m. p. 148°, respectively.) The quinone is oxidised by sodium dichromate in the presence of glacial acetic acid to 4-nitronaphthalene-1 : 8-dicarboxylic acid, the anhydride of which has m. p. 220°. Concentrated potassium hydroxide solution converts the nitroquinone into 4(?5)-nitronaphthaldehydic acid (annexed formula), m. p. 245—247°.



5 : 6-*Dinitroacenaphthene*-1 : 2-*quinone*, m. p. above 300° (slow decomp.), is prepared by the more energetic nitration of acenaphthenequinone, and is oxidised by sodium dichromate in boiling glacial acetic acid solution to the *anhydride* of 4 : 5-*dinitronaphthalene*-1 : 8-*dicarboxylic acid*, m. p. above 300°; the latter substance (m. p. 310°) appears also to be formed by the oxidation of 5 : 6-dinitroacenaphthene. H. W.

Preparation of Aromatic Nitro-compounds of Retene and its Homologues. ROBERT ARNOT (D.R.-P. 315623; from *Chem. Zentr.*, 1920, ii, 188—189).—Retene or retenequinone, or a resin oil of high boiling point, particularly tar tallow, is treated with nitric acid (D greater than 1·43) in the presence or absence of fuming sulphuric acid. *Dinitroretene*, from retene or tar tallow and red, fuming nitric acid or concentrated nitric acid (D 1·48—1·52) at 15°, forms a lemon-yellow, flocculent precipitate; the diazonium compound derived from the corresponding amine yields azo-dyes with suitable components. *Dinitroretenequinone*, from the quinone, gives an olive-green solution in alcoholic alkali, which becomes red when warmed and green again when cooled; the hot alcoholic solution of dinitroretenequinone becomes red on addition of alkali. *Nitroretenesulphonic acid*, from retene, 20% oleum, and nitric acid, forms a yellowish-brown precipitate. H. W.

Fluidities and Volumes of some Nitrogenous Organic Compounds. EUGENE C. BINGHAM, HENRY S. VAN KLOOSTER, and WALTER G. KLEINSPEHN (*J. Physical Chem.*, 1920, **24**, 1—20. Compare A., 1910, ii, 395).—The liquids examined were very carefully purified, and their corrected boiling points are recorded, as follows: benzonitrile 190·7°, o-toluidine 198·2°, aniline 182·7°, diethylaniline 212°, dimethylaniline 192·37° (m. p. 2·1°), ethylaniline 203·6°, methylaniline 194·7°, and nitrobenzene 209·3°; these differ in many cases from the generally accepted values. The density and viscosity have been determined at intervals of 10° over the temperature range 0—100°. The experimental results show that aniline is considerably associated; substitution of groups in the benzene nucleus has but little effect on the association, whilst successive substitution in the amino-group reduces the association progressively. The atomic constant for nitrogen in aniline at a fluidity of 200 is 3·4, but it remains an open question whether it has the same value in nitriles and nitro-compounds. Mixtures of aniline and dimethylaniline follow the additive fluidity rule fairly closely. J. F. S.

Trisulphanilic [Aniline-2 : 4 : 6-trisulphonic] Acid. S. C. J. Olivier (*Rec. trav. chim.*, 1920, **39**, 194—199).—When aniline-*p*-sulphonic acid (100 grams) is heated with 600 c.c. of a mixture of one part of phosphoric oxide and three parts of sulphuric acid at 180° for eight hours, *aniline*-2 : 4 : 6-*trisulphonic acid* is obtained and isolated as its *barium* salt, $[C_6H_2(NH_2)(SO_3)_3]_2Ba_3 + 10H_2O$. The free *acid* crystallises with $4H_2O$, is very hygroscopic, and gives a *sodium* salt, $NH_2{\cdot}C_6H_2(SO_3Na)_3,2H_2O$; a *potassium* salt, $NH_2{\cdot}C_6H_2(SO_3K)_3,H_2O$, and a *potassium hydrogen* salt,

$$NH_2{\cdot}C_6H_2(SO_3K)_2{\cdot}SO_3H.$$

When the acid is diazotised in acid solution with potassium nitrite, or when its potassium salt is diazotised by a current of nitrogen trioxide, it gives a stable diazo-salt, *potassium diazobenzenetrisulphonate*, $(SO_3K)_2C_6H_2{<}{}^{N\colon N}_{SO_3}$, which is only slowly decomposed in Gattermann's reaction, giving 1-*chlorobenzene*-2 : 4 : 6-*trisulphonic acid*, yielding an *acid chloride*, $C_6H_2Cl(SO_2Cl)_3$, m. p. 171—171·5°, which, when heated in a sealed tube with phosphorus pentachloride at 200—210° for three hours, yields 1 : 2 : 4 : 6-tetrachlorobenzene.

If anilinetrisulphonic acid itself is diazotised in alcoholic solution with nitrogen trioxide, it yields, after distilling off the alcohol under reduced pressure, *diazobenzenetrisulphonic acid*,

$$\begin{matrix}N\colon N\\O_3S\end{matrix}{>}C_6H_2(SO_3H)_2,$$

which, when boiled with alcohol, gives benzene-1 : 3 : 5-trisulphonic acid. W. G.

Preparation of Condensation Products from Formaldehyde and Primary Aromatic Amines. Alexander M. Nastukov and Peter M. Croneberg (D.R.-P. 308839; from *Chem. Zentr.*, 1918, ii, 999—1000).—Primary aromatic amines are treated with formaldehyde, preferably in slight excess, in the presence of boiling dilute mineral acids, such as hydrochloric or sulphuric acid; the theoretical yields of amino-bases, free from oxygen and resin and of constant m. p., are thus obtained, which develop on the fibre azo-dyes of red, Bordeaux-red, khaki-brown, or yellow shades. The colours obtained are fast to alkalis, acids, and washing. The *amino-base* from *o*-toluidine, formaldehyde, and sulphuric acid is an amorphous, pale yellow precipitate, m. p. 110—111°. Formaldehyde yields with aniline an amorphous, brownish-yellow *base*, m. p. 114—115°, with technical xylidine a *base*, m. p. 58·5—59·5°, with *o*-anisidine an amorphous, pale yellow *compound*, m. p. 133—134°, and with *m*-toluidine a *base*, m. p. 169—170°. H. W.

Molecular Organic Compounds. III. M. Giua and F. Cherchi (*Gazzetta*, 1919, **49**, ii, 264—285. Compare A., 1917, i, 386).—Investigations have been made on the binary systems formed by diphenylamine with *o*-nitrophenol, *s*-trinitrophenol, azo-

benzene, *n*-cetyl alcohol, 2:4-dichloroaniline, *s*-trichlorophenol, and benzophenone.

The system diphenylamine–*o*-nitrophenol exhibits a single eutectic point at the concentration 51% of the nitrophenol and the m. p. 21·6°. The fused mixtures of the two components show clearly the general phenomenon observed with mixtures of diphenylamine and aliphatic or aromatic nitro-compounds (compare Ciusa and Vecchiotti, A., 1912, i, 755; Pushin and Grebenschtschikov, A., 1913, ii. 105; Tinkler, T., 1913, **103**, 2171; Giua, A., 1915, i, 659; 1916, i, 205; Gomberg and Schoepfle, A., 1917, i, 551), the addition of a small proportion of o-nitrophenol sufficing to impart an intense red coloration to diphenylamine.

The resnlts obtained with the system diphenylamine–*s*-trinitrophenol indicate the formation of a compound which contains the components in the molecular ratio 1 : 1, and dissociates on melting. The intense red coloration persists even after solidification of the mixtures, but gradually changes to a greenish-yellow, which is still evident after the solid mass has remained for some days at about 25° (compare Walker, T., 1896, **69**, 1341).

The system diphenylamine–azobenzene exhibits only one eutectic point. The addition of azobenzene in small proportion to diphenylamine results in an intense dark red coloration, but the formation of an additive compound is excluded. The auxochrome group, ·N:N·, of the azobenzene functions, as regards colour, quite similarly to the nitro-group.

Cetyl alcohol, 2:4-dichloroaniline, and *s*-trichlorophenol show no peculiarities in their behaviour towards diphenylamine, the solidification curves possessing one eutectic point in each case. In the cetyl alcohol system, the solidifying point of diphenylamine is lowered from 53·1° to about 38° by addition of 68·99% of the alcohol; mixtures of the two compounds in the hot form pale yellow solutions. For the system diphenylamine–2:4-dichloroaniline, the eutectic corresponds with the concentration 44% of the aniline, and melts at about 44°; fused mixtures of the two components are colourless.

Benzophenone and diphenylamine combine in the molecular proportions 1:1 to form a pale yellow additive compound, m. p. 30·85°, which must be classed with the molecular compounds containing auxochromes (compare Kauffmann, "Die Valenzlehre," Stuttgart, 1911, 509). The eutectic between the additive compound and diphenylamine has m. p. about 28·7°, and that between the compound and benzophenone m. p. about 24°. T. H. P.

Derivatives of Quadrivalent Nitrogen. HEINRICH WIELAND and KARL ROTH (*Ber.*, 1920, **53**, [*B*], 210—230).—The behaviour of diphenylnitric oxide (Wieland and Offenbächer, A., 1914, i, 955) towards other radicles, such as nitric oxide, nitrogen peroxide, triphenylmethyl, and a derivative of diphenylnitrogen, has been investigated, and the unstable di-*p*-tolylnitric oxide has been prepared and examined in a similar direction.

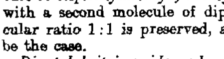
Diphenylhydroxylamine is prepared by a slight modification of the method of Wieland and Roseeu (A., 1912, i, 253), and is transformed into diphenylnitric oxide, m. p. 64° (compare Wieland and Offenbächer, *loc. cit.*), which, when quite pure, can be preserved in ethereal solution during twenty-four hours without undergoing alteration. When its ethereal solution is treated with nitric oxide at 0°, a mixture of *p*-nitrodiphenylnitrosoamine and diphenylnitrosoamine is formed. Apparently the first stage of the reaction consists in the addition of nitric oxide to yield the compound $O{:}NPh_2{\cdot}N{:}O$ (which is analogous to N_2O_3); this probably is converted successively into the isomeric diphenylnitroamine and *p*-nitrodiphenylamine, $Ph_2N{\cdot}NO_2 \longrightarrow NO_2{\cdot}C_6H_4{\cdot}NHPh$; the secondary amine is then converted into its nitroso-derivative according to the scheme:

$$NO_2{\cdot}C_6H_4{\cdot}NHPh + O{:}NPh_2{\cdot}N{:}O \longrightarrow NO_2{\cdot}C_6H_4{\cdot}NPh{\cdot}NO + Ph_2N{\cdot}OH.$$

The diphenylamine, which is isolated as its nitroso-derivative, is formed by the auto-decomposition of diphenylhydroxylamine. That a compound analogous in its action to nitrogen trioxide is actually formed is shown by the fact that if the experiment is repeated in the presence of diphenylamine or di-*p*-tolylamine, the nitroso-derivatives of these substances are formed in large quantity.

Diphenylnitric oxide reacts with triphenylmethyl to yield the *compound*, $Ph_2N{\cdot}O{\cdot}CPh_2{\cdot}C_6H_4{\cdot}CPh_3$, m. p. 160°, the constitution of which is deduced from its catalytic hydrogenation to diphenylamine and the carbinol of Ullmann and Borsum's "hexaphenylethane," which Tschitschibabin (A., 1905, i, 125) has shown to be *p*-benzhydryltetraphenylmethane. The course of the reaction is remarkable, since the simple additive product first formed appears to be so strongly unsaturated that it combines with a second molecule of triphenylmethyl; the hydrogen which is thus liberated reacts with a second molecule of diphenylnitric oxide, so that the molecular ratio 1 : 1 is preserved, as is experimentally demonstrated to be the case.

Di-p-tolylnitric oxide, red needles, m. p. 59—60°, is prepared by oxidising di-*p*-tolylhydroxylamine (Wieland and Roseeu, A., 1915, i, 797) with dry silver oxide; even when placed in a vacuum and removed from light, the substance cannot be preserved for more than three hours; after a few hours it yields a dark, semi-crystalline mass, from which di-*p*-tolylamine can be extracted. With nitric oxide it yields a pale yellow, crystalline, somewhat unstable *compound*, $C_{14}H_{14}O_2N_2$, m. p. 93°, which is not identical with *o*-nitroditolylamine; the substance could not be reduced to ditolylhydrazine or ditolylamine and ammonia, so that it is not ditolylnitroamine. It is provisionally assumed to have the annexed formula.

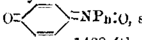


Di-*p*-tolylhydrazine is converted by nitrogen peroxide into 2:2′-dinitrodi-*p*-tolylamine, cinnabar-red needles, m. p. 192—193° (*decomp.*).

Di-p-*nitrophenylnitric oxide*, $(NO_2\cdot C_6H_4)_2N\dot{:}O$, dark red crystals, is prepared by the action of nitrogen peroxide on diphenylnitric oxide, or, more conveniently, on diphenylhydroxylamine. It has m. p. 109° (decomp.) and is remarkably stable, since it can be preserved without change during three months. Its formation probably occurs according to the scheme: $Ph_2N\dot{:}O + NO_2 \longrightarrow O\dot{:}NPh_2\cdot NO_2 \longrightarrow NO_2\cdot C_6H_4\cdot NPh\cdot OH \longrightarrow NO_2\cdot C_6H_4\cdot NPh\dot{:}O \longrightarrow (NO_2\cdot C_6H_4)\cdot NPhO\cdot NO_2 \longrightarrow$

$$(NO_2\cdot C_6H_4)_2N\cdot OH \longrightarrow (NO_2\cdot C_6H_4)_2N\dot{:}O.$$

It is reduced by stannous chloride and hydrochloric acid to 4:4′-diaminodiphenylamine, and by phenylhydrazine to *di*-p-*nitrophenylhydroxylamine*, orange-yellow needles, m. p. 90° (decomp.); the latter is markedly acidic in character and yields two series of salts, giving, for example, with an ethereal solution of phenylhydrazine a pale orange *compound*, m. p. 126° (decomp.), and with aqueous ammonia or with alkalis intensely deep blue solutions. The use of phenylhydrazine as a reducing agent in this connexion is of particular interest, since other agents transform the oxide directly into the secondary amine. Di-*p*-nitrophenylnitric oxide reacts with nitric oxide to yield a substance which has all the properties expected of *di*-p-*nitrophenylnitroamine*; it is, however, decomposed by crystallisation from ethyl acetate, yielding 4:4′-dinitrodiphenylamine, m. p. 213—215°; it combines with triphenylmethyl to yield *NN-di*-p-*nitrophenyl-O-triphenylmethylhydroxylamine*, $(O_2N\cdot C_6H_4)_2N\cdot O\cdot CPh_3$, pale yellow, rhombic platelets, m. p. 180° (decomp.), which is reduced by hydrogen in the presence of palladium-black to 4:4′-diaminodiphenylamine and triphenylcarbinol.

Diphenylnitric oxide is remarkably stable towards water and alkalis, but is rapidly converted by 2*N*-hydrochloric acid into diphenylamine and *quinoneanil oxide*,  shining prisms with a pale brown surface coloration, m. p. 142° (the latter is reduced by zinc dust in glacial acetic acid solution to *p*-hydroxydiphenylamine, which is converted by dry silver oxide into quinoneanil, m. p. 98°). For some unexplained reason, ethereal solutions of diphenylnitric oxide occasionally undergo the same change spontaneously.

The stability of the diarylnitric oxide diminishes from the dinitrophenyl through the phenyl to the di-*p*-tolyl derivative; the stability of the di-*p*-anisyl compound described by Meyer and Gottlieb-Billroth (this vol., i, 38) is therefore remarkable. H. W.

The Transformation of Dinitrophenolsulphonic Acids into Picric Acid. M. Marqueyrol, P. Carré, and P. Loriette (*Bull. Soc. chim.*, 1920, [iv], **27**, 140—143).—The transformation of 2:6-dinitrophenol-*p*-sulphonic acid into picric acid is more rapid

than that of the 2:4-dinitrophenol-*o*-sulphonic acid. It is thus preferable, in the manufacture of picric acid, to use a sulphonated phenol mixture containing the maximum amount of phenol-2:4-disulphonic acid. W. G.

The Preparation of Picric Acid by the Process with Nitric Acid using Nitric Acids of Different Concentrations. M. MARQUEYROL, P. CARRÉ, and P. LORIETTE (*Bull. Soc. chim.*, 1920, [iv], **27**, 143—148).—By arranging completely to utilise the nitric acid used, it is possible to obtain good yields of picric acid by sulphonating 100 grams of phenol with 350 grams of 92·5% sulphuric acid, heating the mixture on a water-bath for three hours, and then nitrating the mixture with five molecular proportions of nitric acid (D 1·273). Under laboratory conditions, it does not seem possible to use less than these proportions of sulphuric and nitric acids. W. G.

Equilibrium Diagrams of Binary Mixtures of Picric Acid, Trinitrotoluene, Dinitrotoluene, and Mononitronaphthalene. A. WOGRINZ and P. VÁRI (*Z. ges. Schiess. u. Sprengstoffw.*, 1919, **14**, 249—251, 267—270; from *Chem. Zentr.*, 1920, i, 115).—The cooling curves have been deduced from experiments performed in a special type of apparatus, which is fully described, and is designed to secure closely similar external conditions. The curves are given for the systems: picric acid–dinitrotoluene, tri- and dinitrotoluenes, trinitrotoluene–nitronaphthalene. H. W.

Modern Shattering Nitro-explosives. C. F. VAN DUIN and B. C. ROETERS VAN LENNEP (*Rec. trav. chim.*, 1920, **39**, 145—177). —The authors have examined nineteen nitro-compounds of different types, capable of being used as explosives, to determine their stability, temperature of explosion, and sensitiveness to mechanical shock, and thus to determine the influence of constitution on these properties.

For the stability test, the Dutch method has been used, which consists in heating 10 grams of the substance in a special flask at 95° first for three hours, and if no decomposition occurs, for eight hours per day up to a period of thirty days. Under these conditions, trinitrophenylmethylnitroamine, trinitroaminophenol, trinitroaminoanisole, trinitroaminophenetole, trinitro-*m*-phenylenediamine, trinitromethylnitroaminophenol, aminotrinitrophenylmethylnitroamine, hexanitrodiphenyl sulphide and sulphone, and dipicrylamine stood the test. Tetranitroaniline showed marked decomposition after twenty-six hours at 60°, whilst tetranitrophenylmethylnitroamine was even less stable, the substance containing the most active nitro-group being thus the least stable. Tetranitrophenol showed signs of decomposition after four hours at 70°. In general, the 2:3:4:6-tetranitro-derivatives decompose rapidly either at high temperatures or at the ordinary temperature, this being probably due to the splitting off of the nitro-group in

position 3. Stettbacher's view (compare *Z. ges. Schiess. u. Sprengstoffw.*, 1916, **11**, 114) that the nitrous acid evolved in the decomposition of tetranitroaniline comes from an action between the amino- and the *o*-nitro-groups is incorrect. The instability of substances with mobile nitro-groups is due to these mobile groups, and a methylnitroamino-group also exerts an unfavourable influence on the stability of a compound.

In determining the temperature of explosion, it is advisable to determine the figure by two methods, one in which the temperature is raised above 100° by 20° a minute, and the second in which it is only raised 5° a minute, in order to get a correct idea of the behaviour of the explosives. There is apparently no definite relationship between the explosion temperature and the stability of a compound. In the case of substances which decompose at their melting point, the decomposition and explosion temperatures are generally almost equal.

For testing such nitro-explosives for their sensitiveness to shock, the authors find Kast's method (compare *Z. ges. Schiess. u. Sprengstoffw.*, 1909, **4**, 263) quite satisfactory. The introduction of a methylnitroamino-group or of a fourth nitro-group notably increases the sensitiveness to shock, whilst an amino-group lowers it. The etherification of a phenol diminishes its sensitiveness. Apart from the nature of an entrant group, its mobility, in the case of highly nitrated substances, exerts a marked influence, mobility increasing sensitiveness. The replacement of a fixed nitro-group by a mobile group produces a remarkable influence on the sensitiveness, as is shown by a comparison of dipicrylamine with 2 : 4 : 6 : 2′ : 3′ : 4′-hexanitrodiphenylamine. W. G.

Esters of *N*-Arylsulphonyl-*N*-alkylaminoaryl Esters. E. Reber and J. Siegwart (U.S. Pat. 1316804).—*N*-Toluenesulphonyl-*p*-aminophenyl *toluenesulphonate* (*A*),

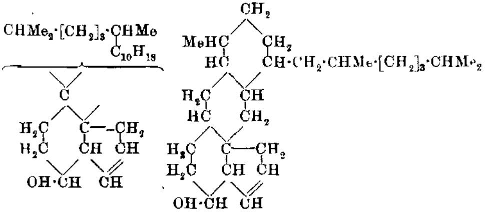
$$C_6H_4Me\cdot SO_2\cdot O\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_6H_4Me,$$

is dissolved in aqueous sodium hydroxide, and, on cooling the hot solution, the sodio-derivative crystallises. This is converted almost quantitatively into the N-*methyl* derivative of *A*, needles, m. p. 162°, by heating for several hours at 100—120° with methyl chloride and methyl alcohol. Other alkylating agents may be used, such as ethyl haloids (m. p. 117°), allyl bromide (m. p. 113°), ethylene dibromide, or benzyl bromide (m. p. 142°), with alcohol or water as diluent (the m. p. of the derivative of *A* prodnced is given in brackets). Corresponding derivatives of *o*- or *m*-aminophenol, or of the aminonaphthols and their substitution products, which are substituted in the amino-group by an arylsulphonyl radicle and in the hydroxyl group by an acyl radicle, can also be easily alkylated. Chemical Abstracts.

Catechol. Benno Elsner (*Monatsh.*, 1919, **40**, 361—362).—At dilutions not greater than 1%, with excess of cold barium hydroxide solution, catechol gives a precipitate of a very sparingly

soluble *barium* salt, $C_6H_4O_2Ba,3\frac{1}{2}H_2O$, in the form of silver-grey leaflets with a pearly lustre. Since resorcinol and quinol do not give such a precipitate, the reaction is suggested as a means of separation, which is probably superior to that which depends on the use of benzene. J. K.

Constitution of Cholesterol. A. WINDAUS (*Nachr. K. Ges. Wiss. Göttingen*, 1919, 237—254; from *Chem. Zentr.*, 1920, i, 82). —The author gives a general account of the investigations which have, in part, served to elucidate the constitution of cholesterol. In comparison with the formulæ of the original communications, the present formulæ are increased by the addition of two atoms of hydrogen, since this alteration has been shown to be necessary for the acid, $C_{26}H_{44}O_3$, obtained by the oxidation of cholestenone by potassium permanganate (compare A., 1917, i, 265). If the presence of an octyl radicle (Windaus and Resau, A., 1913, i, 615) be regarded as established, the constitution of cholesterol may be expressed by formula I:



(I) (II)

Two saturated ring systems must be present in the residue which contains ten carbon atoms, and these probably have certain carbon atoms in common with the rings of formula I. Although complete evidence with regard to certain details is lacking, it is possible to put forward a constitutional formula which gives an approximately accurate picture of the arrangement of the carbon atoms. A possible constitution is shown by formula *II*. H. W.

Solubility of Microbic Acid [*p*-Chlorobenzoic Acid]. R. OTTO (*Konserven Zeit*, 1917, **18**, No. 1; *Landw. Jahrb.*, **52**; *Erg. Bd.* **1**, 85—86; from *Chem. Zentr.*, 1919, iii, 1052—1053). —The solubility of *p*-chlorobenzoic acid is given by Seeger as 1:2500 and by Beilstein as 1:5288; the author finds the acid to be much more sparingly soluble than these figures would indicate, and that 25,000 parts of water do not completely dissolve 1 part of it. Failure to detect the presence of *p*-chlorobenzoic acid in alcohol-free fruit juices which have been treated with microbin is therefore readily explicable. H. W.

Catalytic Preparation of Amides. A. MAILHE and (MME) BELLEGARDE (*Caoutchouc et Guttapercha*, 1919, **16**, 9947—9948; from *Chem. Zentr.*, 1919, iii, 952).—Although aromatic amines react readily with aliphatic and aromatic acids to yield substituted amines, the esters, such as methyl benzoate, can be boiled with aniline for a protracted period without forming an appreciable amount of the amide. It is now shown that substituted amines may be readily produced when an equimolecular mixture of ester and amine is allowed to react in the presence of aluminium oxide or thorium oxide at 480—490°. Amides, but not nitriles, are obtained when a mixture of ammonia and the vapour of an acid anhydride is passed over the same catalysts at 450°, and a similar change is observed when an ester is used in place of the anhydride. At a higher temperature, larger amounts of nitriles are produced in certain circumstances. The following examples are cited. Benzanilide is prepared from aniline and methyl or ethyl benzoate, the yield being 40—50% of the quantity of ester used; the three isomeric benzotoluidides from benzoic ester and the requisite toluidine; *benzocyclohexylamide*, $C_6H_{11}\cdot NH\cdot COPh$, m. p. 153°, from methyl benzoate and *cyclo*hexylamine; phenylpropionanilide; cuminanilide; acetanilide and its homologues from aniline and the corresponding aliphatic esters. The following compounds are obtained by the use of gaseous ammonia. Propionamide and *iso*valeramide from the corresponding anhydrides; salicylamide from methyl salicylate (in this instance the formation of nitrile is not observed if the catalyst is heated to 500°). H. W.

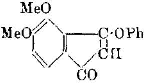
Preparation of New Mono- and Di-β-hydroxyethylaminobenzoic Esters. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 128552).—Mono- and di-β-hydroxyethylaminobenzoic esters are obtained by heating to temperatures varying from 50° to 110° a mixture of ethylene oxide and an aminobenzoic ester in molecular proportion of one or two of ethylene oxide respectively to one of ester. The reaction can be accelerated by the addition of small quantities of water or ethyl alcohol. Thus *ethyl β-hydroxyethyl-p-aminobenzoate*, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2Et$, a colourless, crystalline substance, melting at 63° and boiling at 213—214°/4 mm., is produced by heating for several hours in a closed vessel at 50° equimolecular proportions of ethylene oxide and ethyl *p*-aminobenzoate, whilst if under similar conditions 2 mols. of ethylene oxide are used, together with ½ mol. of water and 1 mol. of ethyl alcohol, *ethyl di-β-hydroxyethyl-p-aminobenzoate*,

$$(OH\cdot CH_2\cdot CH_2)_2N\cdot C_6H_4\cdot CO_2Et,$$

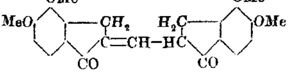
is obtained. After crystallisation from benzene it forms white lamellæ, m. p. 94° and b. p. 246°/4 mm. G. F. M.

2 : 3-Dimethoxyphenylpropiolic Acid and 4 : 5-Dimethoxyhydrindone. S. RUHEMANN (*Ber.*, 1920, **53**, [*B*], 274—284).—Ethyl 2 : 3-dimethoxycinnamate (compare Perkin and Robinson, T., 1914, **105**, 2387; Kranichfeldt, A., 1914, i, 190), colourless

prisms, m. p. 45—46°, b. p. 184—185°/15 mm., is prepared by the action of ethyl acetate and sodium on 2:3-dimethoxybenzaldehyde; it readily absorbs bromine to yield the corresponding dibromo-ester, but, at the same time, a certain amount of hydrogen bromide is invariably eliminated. The crude ester, which could not be purified, is converted by alcoholic potassium hydroxide solution into 2 : 3-*dimethoxyphenylpropiolic acid*, $C_6H_3(OMe)_2{\cdot}C{:}C{\cdot}CO_2H$, colourless prisms, m. p. 108—109°. In a similar manner to 4-methoxy-1-naphthylpropiolic acid (this vol., i, 326), the latter is transformed by alcohol and hydrogen chloride into *ethyl β-chloro-2:3-dimethoxycinnamate*, colourless oil, b. p. 190—191°/12 mm., which, when treated with sodium phenoxide, gives *ethyl β-phenoxy-2:3-dimethoxycinnamate*, pale yellow, viscous oil, b. p. 242—244°/12 mm. Hydrolysis of the latter yields the two stereoisomeric *β-phenoxy-2:3-dimethoxycinnamic acids*, coarse, colourless crystals, m. p. 192—193° (decomp.), and silky needles, m. p. 137—138°, respectively, which can be comparatively readily separated by fractional crystallisation from alcohol. Instead of the expected flavone, either isomeride, when acted on by phosphorus pentachloride and aluminium chloride successively, yields 3-*phenoxy-4:5-dimethoxyindone* (annexed formula), colourless, shining leaflets, m. p. 199—200°, the constitution of which is deduced from its conversion by hydriodic acid into phenol and 4 : 5-*dihydroxyindane-1 : 3-dione*, colourless needles, m. p. 277—278° (decomp.), the white, unstable *silver* salt of which is also described.

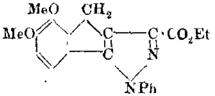


4:5-Dimethoxy-1-hydrindone, yellow leaflets, m. p. 77—78° (Perkin and Robinson, T., 1914, **105**, 2388, give 82°), is conveniently prepared from 2:3-dimethoxy-β-phenylpropionic acid by the successive action of phosphorus pentachloride and aluminium chloride. Attempts to convert it into an azomethine by the action of *p*-nitrodimethylaniline and potassium hydroxide were unsuccessful, the alkali affecting almost exclusively the nitroso-base and forming pp′-*tetramethyldiaminoazoxybenzene*, yellowish-brown needles, m. p. 239—240°. 4:5-*Dimethoxy-2-hydroxymethylene-1-hydrindone*, almost colourless needles, m. p. 135—136°, after softening at 130°, is prepared by the action of sodium and ethyl formate on the hydrindone; the *copper* salt, greenish-yellow powder, and the *anilide*, $C_{11}H_{10}O_3{:}CH{\cdot}NHPh$, yellow prisms, m. p. 168°, are described. When the hydroxymethylene compound is heated at 160° it loses formic acid and yields a *compound* (annexed formula), red prisms, m. p. 222°.



Ethyl oxalate condenses with 4:5-dimethoxy-1-hydrindone in the presence of sodium ethoxide, yielding *ethyl* 4:5-*dimethoxy-1-*

hydrindoneglyoxylate, yellow needles, m. p. 132—133°, from which the corresponding *acid*, yellow needles, m. p. 232°, is obtained in the usual manner. The ester reacts readily with phenylhydrazine hydrochloride in the presence of a few drops of concentrated hydrochloric acid, giving *ethyl* 7 : 8-*dimethoxy*-1-*phenylindeno*-2′ : 3′ : 4 : 5-*pyrazole*-3-*carboxylate* (annexed formula), colourless, silky needles, m. p. 172—173°; the corresponding acid forms slender needles, m. p. 240—241° (*decomp.*). H. W.



Ethyl Diphenyleneacetate. S. Ruhemann (*Ber.*, 1920, **53**, [*B*], 287—289).—The sodio-derivative of ethyl fluorene-9-dicarboxylate (Wislicenus and Mocker, A., 1913, i, 1187) reacts with ethyl phenylpropiolate to yield carbon dioxide and *ethyl β-diphenylenemethylcinnamate*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!CH{\cdot}CPh{:}CH{\cdot}CO_2Et$, yellow crystals, m. p. 98—99°; the corresponding *acid* crystallises in yellow leaflets, m. p. 219—220°, and is reduced by sodium amalgam to *β-diphenylenemethyl-β-phenylpropionic acid*, colourless prisms, m. p. 184—185°. H. W.

Regularities Observed in the Pyrogenic Degradation of certain Cyclic Hydroxy-acids of the Benzene Series. Hermann Kunz-Krause and Paul Manicke (*Ber.*, 1920, **53**, [*B*], 190—201). —When salicylic acid is rapidly heated to a temperature not exceeding 250°, it loses carbon dioxide and water, but only 46·39% of it is converted into phenyl salicylate; at temperatures between 250° and 350°, carbon dioxide is evolved in regularly increasing amount, and, above 280°, the formation of phenol in small quantity can be detected. When rapidly distilled, the acid (contrary to the generally accepted views) does not undergo an even partial, smooth conversion into carbon dioxide and phenol; the product only contains very small quantities of the latter in addition to salol and other substances. Similar experiments with protocatechuic acid (3 : 4-dihydroxybenzoic acid) show that a smooth decomposition into catechol and carbon dioxide does not occur between 200° and 300°. Rapid distillation of protocatechuic acid yields carbon dioxide, catechol, and tetrahydroxyanthraquinone (rufiopine). Gallic acid, on the other hand, is quantitatively converted at 240—245° into carbon dioxide and pyrogallol or Pelouze's melangallic acid; when rapidly distilled it yields 1 : 2 : 3 : 5 : 6 : 7-hexahydroxyanthraquinone. The formation of derivatives of anthracene from benzene compounds by a purely pyrogenic action is of interest in that it affords a possible explanation of the occurrence of compounds of the two series in coal tar. H. W.

Syntheses of Naphthyl-lactic and Naphthylcinnamic Acids. II. β-Phenyl-β-2-naphthyl-lactic Acid. Remo de Fazi (*Gazzetta*, 1919, **49**, ii, 250—253. Compare A., 1919, i, 529).—*β-Phenyl-β-2-*

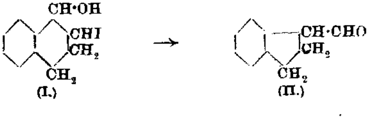
naphthyl-lactic acid, $C_{10}H_7·CPh(OH)·CH_2·CO_2H$, obtained as ethyl ester by decomposing by means of acidified water the complex formed by the interaction of phenyl β-naphthyl ketone and ethyl bromoacetate in benzene solution in presence of zinc dust, forms slender, white needles, m. p. 225—226°, and with concentrated sulphuric acid gives an emerald-green coloration, which immediately changes to yellowish-brown with intense green fluorescence. The *ethyl* ester forms white laminæ, m. p. 114—115°, and with concentrated sulphuric acid gives an intensely green solution showing marked green fluorescence. T. H. P.

Phthaleins and Fluorans. MAURICE COPISAROW (T., 1920, **117**, 209—218).

Preparation of *p*-Dimethylaminobenzaldehyde. T. INGVALDSEN and L. BAUMAN (*J. Biol. Chem.*, 1920, **41**, 145—146).—The authors modify the method of Ullmann and Frey (A., 1904, i, 423) by omitting the isolation of the hydrochloride of the benzylidene compound prepared by the condensation of *p*-nitrosodimethylaniline and *p*-dimethylaminobenzyl alcohol, and decomposing the free base by formaldehyde and acetic acid at the ordinary temperature. The crude aldehyde is purified by distillation in a partial vacuum. J. C. D.

The Iodhydrin Derived from Cinnamyl Methyl Ether. HENRI BEAUFOUR (*Bull. Soc. chim.*, 1920, [iv], **27**, 148—152. Compare A., 1912, i, 621; 1913, i, 466, 467).—The iodohydrin obtained by treating cinnamyl methyl ether with iodine and mercuric oxide (*loc. cit.*), when slowly added in ethereal solution to an aqueous solution of silver nitrate (compare Tiffeneau, A., 1907, i, 922), gives *methyltropaldehyde*, $OMe·CH_2·CHPh·CHO$, b. p. 217—218°, D^0 1·0711, giving an *oxime*, b. p. 175°/15 mm., D^0 1·121, and a *semicarbazone*, m. p. 125°. On oxidation it yields *methyltropic acid*, m. p. 63°, b. p. 177—180°/15 mm., giving an *ethyl* ester, b. p. 139—140°/10 mm. or 250—251°/765 mm., D^0 1·0724. Attempts to prepare the corresponding primary alcohol by reduction of this ester were not successful, the main product, in every case, being atropic acid. W. G.

Phenylic Transposition in the Tetrahydronaphthalene Series. M. TIFFENEAU and A. ORÉKHOFF (*Compt. rend.*, 1920, **170**, 465—467).—The iodhydrin of αβ-tetrahydronaphthalene glycol (I), when treated with silver nitrate in ethereal solution, undergoes phenylic transposition, giving *hydrindene-2-aldehyde*



(I.) (II.)

(formula II), b. p. 135°/30 mm., D^0 1·095, giving a *semicarbazone*, m. p. 167°, an *oxime*, m. p. 104°, and a *bisulphite* compound.

Neither the iodhydrin of $\beta\beta$-tetrahydronaphthalene glycol nor the iodhydrin of hydrindene glycol undergoes this transposition when similarly treated with silver nitrate. W. G.

The Beckmann Rearrangement. IX. Action of Phosphorus Pentasulphide on Benzophenoneoxime. MITSURU KUHARA and KÔZÔ KASHIMA (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1919, **4**, 69—75. Compare A., 1918, i, 179).—Dodge (A., 1891 1238) and Ciusa (A., 1906, i, 953) have observed that thiobenz anilide is formed when benzophenoneoxime is warmed with phos phorus pentasulphide, and have ascribed this change to the Beck mann rearrangement of thiobenzophenoneoxime, formed accordin to the equation $5CPh_2{:}N{\cdot}OH + P_2S_5 = 5CPh_2{:}N{\cdot}SH + P_2O_5$. I analogy with Kuhara's previous studies of this transformation, i is now found that the rearrangement is due to the formation of a ester of the thio-oxime, for when the reaction is carried out i ethereal suspension, *thiobenzophenoneoxime hydrogen phosphate* $OH{\cdot}PO(SN{:}CPh_2)_2$, is obtained as a fibrous, greenish-yellow mass which changes into thiobenzanilide with almost explosive violenc at 70°. A more stable derivative is obtained by treating this este with cold, alcoholic potassium hydroxide, the product being *thio benzophenoneoxime dipotassium hydrogen orthophosphate*,

$$OH{\cdot}PO(OK)_2(SN{:}CPh_2)_2,$$

a white, crystalline powder which changes into thiobenzanilide a 149°. J. C. W.

Zinc Chloride as a Condensing Agent. V. Condensatio Products of Aniline and Hydroaromatic Ketones. (REDDELIEN and O. MEYN (*Ber.*, 1920, **53**, [*B*], 345—354. Compar A., 1914, i, 698, and following abstract).—It has been shown prev ously that aniline zincichloride powerfully catalyses the condens tion of ketones with amines, and is the only useful agent in th cases of enolisable ketones containing the group $\cdot CO\cdot CH_2\cdot$ and unsaturated ketones of the type $>C{:}C{:}CO$. It is now found to b applicable to hydroaromatic ketones.

cyclo*Hexanoneanil*, pale yellow oil, b. p. 140°/19 mm., is o tained by heating *cyclo*hexanone, aniline, and aniline zincichlori at 155° during twenty minutes; with other condensing agent such as aniline hydrochloride, extensive auto-condensation and co siderable resinification take place, and non-uniform products very high boiling point are formed. *cyclo*Hexanoneanil is a rea tive substance which undergoes auto-condensation, yielding the *su stance*, $C_{18}H_{23}N$, b. p. 212—214°/18 mm., which regarded as cyclo*hexylidene*-2-cyclo*hexanonean* (annexed formula), since, when treated with dilu acids, it gives aniline and *cyclo*hexylidene-2-*cyc* hexanone (compare Wallach, A., 1907, i, 220; Ma nich, A., 1907, i, 205). The condensed anil is the main product he action of aniline on *cyclo*hexanone in the presence of anili

NPh

zincichloride at 180° for three-quarters of an hour, and can also be prepared by heating *cyclo*hexanoneanil with aniline hydrochloride for a few minutes at 200°. At a higher temperature it also undergoes auto-condensation, and yields aniline and an *anil*, possibly $C_{18}H_{26}$:NPh, dark yellow oil, b. p. 240—250°/14 mm.

Similarly, menthone yields *menthoneanil*, yellow oil, b. p. 159—160°/12 mm.; *menthone-p-toluil*, yellow oil, b. p. 178°/16 mm.; and *menthone-p-anisil*, colourless crystals, m. p. 61·5°, b. p. 195°/16 mm. These substances cannot be preserved for any length of time in contact with air, since they become oxidised and darken in colour. Condensing agents other than aniline zincichloride yield dark brown, resinous oils.

Among unsaturated hydroaromatic ketones, pulegone yields a normal *anil*, yellow oil, b. p. 148—152°/12 mm., and, in addition, *7-anilinomenthone*, b. p. 154—158°/13 mm., and *7-anilinomenthoneanil*, b. p. 153—156°/18 mm.; the latter substances are probably formed by simple addition of aniline to pulegone and pulegoneanil respectively by a process which is not infrequently associated with the action of amines on substances having conjugated double bonds. Dihydrocarvone, on the other hand, yields the *anil*, yellow oil, b. p. 170—171°, very smoothly and without noticeable formation of by-products. *Carvoneanil*, pale yellow oil, b. p. 180—182°/17 mm., is remarkably readily prepared, reaction occurring to some extent between the components at 160° in the absence of catalyst. Camphor, on the other hand, did not react with aniline itself, and only to a small extent in the presence of aniline zincichloride; *camphoranil*, yellow oil, b. p. 164·5—166°/15 mm., m. p. 13·5°, could be obtained in 64% yield by the use of aniline hydrochloride as condensing agent.

Solution of the anils of the unsaturated hydroaromatic ketones in concentrated sulphuric acid gives an intense blue coloration with nitric acid. The reaction is as sensitive as the brucine test. It is shown by carvoneanil, pulegoneanil, and dihydrocarvoneanil (in order of decreasing sensitiveness), but not by *cyclo*hexanoneanil menthoneanil, or camphoranil. The action thus appears to depend on the presence of the group >C:C·C:NPh. The presence of the anil group is shown to be essential, since the coloration is not given by carvonephenylhydrazone. Nitrite, chlorate, chromate, and hydrogen peroxide also yield the colour, which therefore depends on oxidation. H. W.

Condensation Products from Benzylamine and Aromatic Ketones. G. Reddelien (*Ber.*, 1920, **53**, [*B*], 334—340).—It has been shown previously (A., 1913, i, 1203) that hydrogen haloids are frequently effective catalysts in promoting the action of aromatic ketones with amines to form ketoneanils; it is now shown that benzophenonebenzylimide, CPh_2:N·CH_2Ph, m. p. 60—61°, is readily obtained from benzophenone and benzylamine at 180° in the presence of a few drops of hydrobromic acid solution; Hantzsch and Hornbostel (A., 1898, i, 195) have previously prepared the same

substance from benzophenone dichloride, since they found that ketone and amine did not react to an appreciable extent with another even at an elevated temperature. Acetophenonebenimide, transparent needles, m. p. 44·5°, can be obtained in proved yield from the ketone and amine by a slight modificatio the procedure of Hantzsch and Hornbostel (*loc. cit.*); when, h ever, the condensation is effected in the presence of $ZnCl_2,2NH$ hydrobromic acid an entirely different substance is obtained, wh is identified as *2:4:6-triphenylpyridine*, and is shown to be ide cal with the product prepared from benzylidenediacetophenone hydroxylamine by Wislicenus and Newmann (A., 1899, i, 61), fr acetophenone and ammonia in the presence of phosphoric o (Engler and Heine, this Journ., 1873, 1036; Riehm, A., 18 599), and by the distillation of acetophenone ammonia (Thomas, 1907, i, 138). The substance behaves as a very feeble base, when crystallised from concentrated hydrochloric acid, give *hydrochloride*, which somewhat rapidly loses hydrogen chlo when preserved; it separates as unchanged base from its solutio more dilute acid. The formation of triphenylpyridine from ac phenonebenzylimide is accompanied by that of benzylamine dibenzylamine and methane. H. W

Catalytic Action of Hydrogen Haloids in Condensatio II. The Decomposition of Anils. G. REDDELIEN (*Ber.*, 19 **53**, [*B*], 355—358).—It has been shown previously (A., 19 i, 1203) that hydrogen haloids are effective catalysts in the for tion of anils from ketones and aniline, and emphasis has been l on the necessity of a vigilant control of the temperature of reaction if the formation of by-products in large amounts is to avoided. Further investigation now shows that the anils decomposed when heated with aniline hydrobromide. Th benzylideneaniline, when distilled with the addition of a small qu tity of dry aniline hydrobromide, gave aniline, toluene, a acridine, in addition to much brown, resinous matter. A somew similar behaviour was observed with fluorenoneanil and benzildia which evolved aniline at above 200°; benzophenoneanil, on other hand, appeared to be stable.

The possibility of utilising the elimination of aniline for the c densation of anils with reactive hydrocarbons has also been inve gated. Benzophenoneanil and diphenylmethane scarcely reac with one another. Benzophenoneanil and fluorene did not re below 300°, but, after addition of a small quantity of aniline hyd bromide, aniline was readily evolved at 270°, and a hydrocarb was obtained which was identified as bisdiphenylene-ethane inste of the expected diphenyldiphenylene-ethylene, whilst bis phenylene ethylene was also formed in minor quantity. Fluor oneanil and fluorene yielded a similar mixture of hydrocarbons. H. W

Indones. III. 3-Phenylindone and Diphenyltruxon LEMO DE FAZI (*Gazzetta*, 1919, **49**, ii, 253—263. Compare A., 19 063; 1916, i, 151).—*ββ*-Diphenyl-lactic acid does not g

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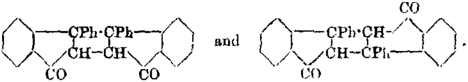
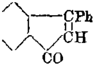
}-phenylindone when treated with phosphoric oxide, but its ethyl ester yields with sulphuric acid the emerald-green coloration regarded by the author as characteristic of those derivatives of lactic and cinnamic acids which are capable of furnishing indones. The green solution is found to contain: (1) a small proportion of an orange-red compound which, in acetic acid solution containing palladium-black, absorbs hydrogen forming 3-phenylhydrindone, and must therefore be 3-phenylindone; (2) considerable proportions of two colourless compounds, $C_{30}H_{20}O_2$, which are dimerides of 3-phenylindone, do not combine with chlorine or bromine, and give no coloration with sulphuric acid; they are therefore regarded as isomeric diphenyltruxones (compare Liebermann, A., 1898, i. 662), having the probable constitutions:



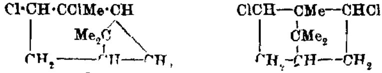
3-Phenylindone (annexed formula) forms an orange-red powder, m. p. 69—71°, and gives an emerald-green coloration with sulphuric acid.



The two *diphenyltruxones* form (1) large, cubical crystals, m. p. 252—253°, and (2) shining, transparent, white prisms, m. p. 209—211°. Both have the normal molecular weights in boiling chloroform. In acetic acid or alcoholic solution, isomeride (2) does not absorb hydrogen in presence of palladium-black, but in acetic acid isomeride (1) slowly absorbs hydrogen, giving a *compound*, $C_{30}H_{24}O_2$, which forms shining, white scales and does not melt at 275°; in this compound the two carbonyl groups of the diphenyltruxone are converted into CH(OH) groups. T. H. P.

Some Derivatives of Fisetol. WILLIAM KERSHAW SLATER and HENRY STEPHEN (T., 1920, **117**, 309—319).

Chlorination of Pinene. OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1915, **57**, 14 pp.; from *Chem. Zentr.*, 1918, ii, 952—953).—The chlorination of pinene in the absence of moisture at −15° to 0° has been investigated; the results differ from any previously recorded. Chlorination occurs in a highly complex manner. The first fractions of the product give abundant solid deposits of pinene hydrochloride. From the higher fractions only a *pinene dichloride* (? II) was obtained, which may have been formed from a primary,



I. II.

*m**

normally formed, unstable dichloro-additive compound (I). It forms transparent, rhombic, bipyramidal, plate-like crystals, m. p. 173—174°, b. p. ca. 130°/10 mm. In addition, a liquid dichloride, b. p. ca. 120—125°/10 mm., which could not be isolated in the pure condition, is also produced. Neither dichloride is affected by boiling aniline.

Preliminary experiments show that pinene hydrochloride can be readily chlorinated in chloroform or carbon tetrachloride solution until four additional atoms of hydrogen have been replaced. Colourless, crystalline products, m. p.'s 135°, 150—152°, and 130° respectively, have thus been obtained, analyses of which give results intermediate between those required for $C_{10}H_{15}Cl_3$ and $C_{10}H_{14}Cl_4$; the formation of a dichloride was not observed. H. W.

The Relative Power of Addition of Unsaturated Compounds. OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1916, **58**, 9 pp.; from *Chem. Zentr.*, 1919, ii, 953).—The action of pinene on different terpene hydrochlorides, particularly at elevated temperature, regularly occurs in such a manner that hydrogen chloride is withdrawn from the latter and ordinary pinene hydrochloride (bornyl chloride) is produced; this is demonstrated in the cases of dipentene dihydrochloride, sylvestrene dihydrochloride, camphene hydrochloride, and dipentene monohydrochloride. Pinene can even remove hydrogen chloride slowly from dry aniline hydrochloride or ammonium chloride. Nopinene and the bicyclic terpene, b. p. 163—165°, recently isolated from Finnish oil of turpentine and provisionally termed γ-pinene, behave similarly to ordinary pinene. In like manner, hydrogen bromide is removed by pinene from camphene hydrobromide or dipentene dihydrobromide. When heated with aniline sulphate and acetic acid, pinene gives *iso*bornyl acetate. On account of its unsaturated nature, pinene behaves in this respect as a base. Even with complex halogen additive products, such as dipentene tetrabromide, pinene effects the removal of halogen acid. This behaviour of pinene and analogous substances is probably attributable to the relatively great latent heat of these terpenes. H. W.

Preparation of Organic Camphol Esters and of Borneol from them in the Presence of Sulphoricinic Acid, which Acts as a Solvent for Camphene or Pinene Hydrochloride. ANDRÉ DUBOSC (*Caoutchouc et Guttapercha*, 1918, **15**, 9555; from *Chem. Zentr.*, 1920, i, 115).—The difficulty of preparing organic camphol esters lies, in part, in the sparing solubility of the substances to be esterified in the acids used; it is now shown that solution can be effected by the addition of sulpho-compounds, particularly of sulphoricinic acid, and that these do not take further part in the action. The separation of ester from sulphoricinic acid and from excess of the acid under esterification occurs in the usual manner. The corresponding camphor alcohols may be obtained by hydrolysis of the esters. H. W.

New Hydrocarbons of High Molecular Weight from Isoprene. OSSIAN ASCHAN (*Öfvers. Finska Vet. Soc.*, 1916, **58**, 42 pp.; from *Chem. Zentr.*, 1918, ii, 954—955).—The additive capacity of caoutchouc shows that one double bond of isoprene disappears in its formation, and is utilised in uniting the condensed isoprene molecules. The molecules which are thus formed by purely chemical reaction are subsequently united to greater complexes, probably by physical and secondary chemical forces (such as residual affinities). According to the author, therefore, two processes are operative in the formation of caoutchouc, which differ from one another not only in respect of rapidity, but also of nature, namely, first, a purely chemical condensation involving certain ethylenic bonds in isoprene and leading to new carbon compounds, and, secondly, formation of greater complexes from the "simplest caoutchouc molecules" so formed which does not involve the production of carbon compounds in the ordinary sense. The latter process only takes place gradually, and is probably never complete; it constitutes the so-called polymerisation of caoutchouc. The converse process, depolymerisation, occurs when caoutchouc forms additive products and when it is dissolved, particularly in hot solvents.

The properties of caoutchouc tetrabromide show it to have a molecular weight which cannot be estimated by the ebullioscopic method. The formation of the complex molecule cannot, however, be a subsequent operation, since the additive product is itself saturated. Bromine is added at the double bonds which remain after or are formed during the polymerisation of isoprene, and in proportion as addition proceeds at the "simplest caoutchouc molecules" the powers of complex formation, present in the caoutchouc, are placed out of action; the state of division of the substance probably remains at the stage corresponding with the "simplest caoutchouc molecules." According to this view, the molecules of caoutchouc and its bromide are both large, but of different orders of magnitude. The tetrabromide is therefore actually amorphous, but has not the viscous consistency of caoutchouc, which indicates a very high molecular weight. The same may be said for most of the other additive products of rubber. In experimental confirmation of the view that the synthesis of caoutchouc takes place in two stages, it is shown that isoprene condenses with other hydrocarbons containing an ethylenic linking, such as amylene (β-methyl-Δ^{β}-butylene), pinene, camphene, and with itself, yielding compounds of very high molecular weight which are amorphous, but do not possess the physical properties of caoutchouc. Both the course of the reaction and the mode of action of the necessary catalyst ($AlCl_3$) indicate that the process is one of actual condensation which proceeds to completion. The products are still unsaturated, but add much less bromine than does caoutchouc. Two different classes of compounds are invariably formed, both of which are solid, but of which the one (*A* product) is completely insoluble in all solvents, whilst the other (*B* product) dissolves in most organic media with

the exception of alcohol. Isomerism probably depends on difference in molecular weight.

A large number of individual experiments are described in the original which do not lend themselves to abstraction. Commercial isoprene yields two different *products* with aluminium chloride; both have the *composition* $(C_{10}H_{18})_n$, but, as was found subsequently, the nature varies with differing proportions of isoprene and amylene. The consecutive products obtained by the step-wise condensation with aluminium chloride have the same percentage composition. Soluble and insoluble substances are alike unsaturated, and have almost identical additive powers. Pure isoprene and pure β-methyl-Δ^{β}-butylene, when separately treated with aluminium chloride, give products of a completely different type. Experiments with mixtures of the two showed that practically only the isoprene of the mixture was acted on if the proportion of amylene was small and the action was cautiously performed. The condensation products must therefore be regarded as polymerised isoprenes. They are not identical, but isomeric, with caoutchouc. Oily substances are obtained as by-products of these condensations, which are possibly synthetic hydrocarbons of the sesqui-, di-, and poly-terpene series. It is further shown that isoprene can be condensed with pinene and camphor to products similar to those formed with β-methyl-Δ^{β}-butylene; it condenses, in addition, with *iso*pinene, dipentene, and sylvestrene. H. W.

Digitalis Substances. XL. H. KILIANI (*Ber.*, 1920, **53**, [*B*], 240—250).—In a previous communication (A., 1919, i, 214), the author has described the degradation of digitogenic acid into a lactone, $C_8H_{12}O_2$, and a monobasic acid. Further examination of the former and the preparation of an *acetyl* derivative, m. p. 89—90°, lead to the adoption of the formula $C_{12}H_{18}O_3$, and this is confirmed by a study of the *magnesium* salt of the corresponding acid. It is also found that the lactone contains 10—15% of a *substance*, $C_{12}H_{18}O_3$, m. p. 76°, which is not dissolved by boiling dilute aqueous alkali, and that the lactone cannot be recovered as such from its solutions in alkali. Revision of the formula of the lactone necessitates alteration in that of the monobasic acid, which should have the composition $C_{16}H_{26}O_5$; re-examination of the product shows that it is not homogeneous, but contains ethyl hydrogen digitogenate, after removal of which, however, the acid still does not conform to the expected formula.

Digitaligenin has $[\alpha]_D$ +454° in 95% alcohol, +443° in alcohol, whilst the hydro-product (A., 1919, i, 91) has $[\alpha]_D$ +42° in 95% alcohol; contrary to the previous statement, the latter yields only a monoacetyl derivative, m. p. 165°. Digitaligenin is converted by fi formic acid in the presence of sodium formate into a *monoformyl* nar derivative, leaflets, m. p. 169°; and is not hydrolysed by treatment hydroth hot dilute alcoholic hydrochloric acid.

gitoxigenin is not hydrolysed by 2% hydrochloric acid, but is ted into a *substance*, $C_{22}H_{32}O_4$, m. p. 175°; *acetyldigitoxigenin*

forms short, coarse rods, m. p. 211—212°. Cautious oxidation of digitoxigenin by chromic acid converts it into a crystalline substance, $C_{19}H_{26}O_4$, which is converted by alcoholic hydrochloric acid into toxigenone, m. p. 260°; the latter is slowly transformed by hot alcoholic sodium hydroxide solution into an amorphous sodium derivative, and hence, contrary to previous statements, appears to have lactonic character.

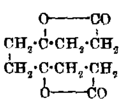
Sodium dixgeninate is oxidised by cold potassium permanganate solution, yielding an *acid*, $C_{17}H_{24}O_6,1{\cdot}5H_2O$, platelets, m. p. 218—219°, $[\alpha]_D$ −31·4°, as potassium salt (the *calcium* salt, $C_{17}H_{12}O_6Ca,1{\cdot}5H_2O$ was analysed); the acid is not affected by an excess of hot sodium hydroxide solution or by cold permanganate, and only slowly by hot permanganate. On the other hand, it is very susceptible to hot hydrochloric acid, which converts it into an *acid*, needles, m. p. 120°, equivalent ca. 300. It is converted by nitric acid into an *acid*, which becomes discoloured at 235° and has m. p. 270° (decomp.); the *calcium* salt was analysed. The investigation of these acids is not yet complete. H. W.

A New Glucoside Hydrolysable by Emulsin: Scabiosin. Em. Bourquelot and M. Bridel (*Compt. rend.*, 1920, **170**, 486—491).—The roots of *Scabiosa succisa*, L., contain sucrose, obtainable in a crystalline form, and also a new glucoside, *scabiosin*, $[\alpha]_D$ −106·52°, which, when hydrolysed by emulsin or by dilute sulphuric acid, gives dextrose and a yellow substance insoluble in water. W. G.

Tetrahydroanemonin. Y. Asahina and M. Atsumi (*J. Pharm. Chim.*, 1920, [vii], **21**, 135—136).—Tetrahydroanemonin, $C_{10}H_{12}O_4$, when treated with sodium ethoxide in alcoholic solution, gives a *sodium* salt, $C_{10}H_{14}O_6Na_2$, very soluble in water, and no longer possessing the ketonic function of anemonin. When acidified, the sodium salt gives, not an acid, but tetrahydroanemonin, which therefore seems to be the dilactone of an unstable acid. The constitutions assigned to this acid and the tetrahydroanemonin are given by formulæ I and II:

$$\begin{array}{l} CH_2{\cdot}C(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \\ CH_2{\cdot}C(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \end{array}$$

(I.)



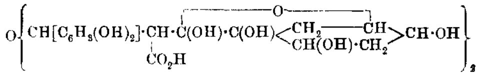
(II.)

The sodium salt, on oxidation in neutral solution with potassium permanganate, yields the sodium salt of anemonolic acid, $CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$. W. G.

Use of Butyl Alcohol as a Solvent for Anthocyanins. Otto Rosenheim (*Biochem. J.*, 1920, **14**, 73—74).—Butyl alcohol removes all the anthocyanins from their solutions in dilute acids. Comparative tests show that the monoglucosides, chrysanthemin

and oenin, are four times as soluble in butyl alcohol as in amyl alcohol; idaein is ten times as soluble. Of the rhamno-glucosides, prunicyanin is sixteen times as soluble, and violanin is twenty-five times as soluble, as in amyl alcohol. Butyl alcohol, therefore, is a suitable solvent for use in the preparation of these substances in the pure condition. The author has prepared pure specimens of *oenin from grapes and pure idaein from cranberries by means of* this solvent. J. F. S.

Tannins. III. Chlorogenic Acid, the Tannin-like Constituent of Coffee. KARL FREUDENBERG (*Ber.*, 1920, **53**, [*B*], 232—239).—Chlorogenic acid has been extensively investigated by Gorter (A., 1911, i, 221, and previous abstracts), who has assigned to it the annexed formula:



This is not easily reconciled with the production of caffeic acid from it under the influence of *Mucor* or *Penicillium* varieties. Repetition of the fission experiments, using tannase, has shown that chlorogenic acid yields caffeic and quinic acids. It has also been found that chlorogenic acid, which Gorter considered to be anhydrous, actually contains $\frac{1}{2}H_2O$; this accounts for the difference between it and the hypothetical hemichlorogenic acid. Chlorogenic acid thus appears simply as a depside of caffeic and quinic acids, and, as appears from Gorter's experiments, the carboxy-group of caffeic acid is united to a hydroxy-group of quinic acid, as indicated by the formula

$$C_6H_3(OH)_2\cdot CH{:}CH\cdot CO\cdot O\cdot C_6H_7(OH)_3\cdot CO_2H.$$

H. W.

The Action of Sodium Hypochlorite on Amides. I. J. RINKES (*Rec. trav. chim.*, 1920, **39**, 200—207).—Sodium hypochlorite acts on $\alpha\beta$-unsaturated amides in the presence of methyl alcohol to give urethanes, which, when hydrolysed with dilute sulphuric acid, yield saturated aldehydes, containing one atom less of carbon than the original amide.

Furylacrylamide, $C_4H_3O\cdot CH{:}CH\cdot CO\cdot NH_2$, under these conditions yields *furylvinylurethane*, $C_4H_3O\cdot CH{:}CH\cdot NH\cdot CO_2Me$, m. p. 102°, which on hydrolysis gives *furylacetaldehyde*, $C_4H_3O\cdot CH_2\cdot CHO$, giving a p-*nitrophenylhydrazone*, m. p. 126°, and a *semicarbazone*, m. p. 130°.

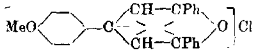
Cinnamaldehyde condenses with cyanoacetic acid to give α-cyanocinnamenylacrylic acid, which, when heated with copper powder, yields cinnamenylacrylonitrile, and this when allowed to remain in contact with fuming hydrochloric acid and ether, gives cinnamenylacrylamide. This amide, with sodium hypochlorite and methyl alcohol, yields *cinnamenylvinylurethane*,

$$CHPh{:}CH\cdot CH{:}CH\cdot NH\cdot CO_2Me,$$

m. p. 134—135°, which is hydrolysed by sulphuric acid to β-*benzylidenepropaldehyde*, CHPh:CH·CH_2·CHO, giving a p-*nitrophenylhydrazone*, a *semicarbazone*, m. p. 192° (decomp.), and an *oxime*, m. p. 117°. W. G.

Pyrylium Compounds. VI. Quino-pyran Derivatives. W. DILTHEY and R. TAUCHER (*Ber.*, 1920, **53**, [*B*], 252—260).—In extension of the work of Dilthey (A., 1919, i, 413), pyrylium salts having a methoxy- or hydroxy-group in the *para*-position in the phenyl group in position "4" have now been prepared which are found to be closely analogous to the corresponding salts in which the α-phenyl group is similarly substituted.

Anisylidenediacetophenone, OMe·C_6H_4·CH(CH_2·CO·C_6H_5)$_2$, colourless, coarse crystals, m. p. 105°, is prepared by the condensation of anisaldehyde and acetophenone with sodium hydroxide in boiling aqueous alcoholic solution; a second *modification*, long, shining crystals, m. p. 93°, is also described, which passes into the former when crystallised from benzene. The *disemicarbazone* forms colourless crystals, m. p. 246—247°. Anisylidenediacetophenone (or a mixture of anisylideneacetophenone and acetophenone) is converted by hydrated ferric chloride in acetic anhydride solution into the *iron* salt of 2:6-diphenyl-4-*p*-anisylpyrylium chloride (annexed formula), small, yellow needles, m. p. 226°, which is transformed by sodium acetate



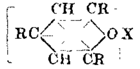
in dilute aqueous solution into *α-hydroxy-ε-keto-αε-diphenyl-γ-*p*-anisyl-Δ^{αγ}-pentadiene*, OH·CPh:CH·C(C_6H_4·OMe):CH·COPh, slender needles, m. p. 122° (*disemicarbazone*, colourless crystals, m. p. 218°; *picrate*, reddish-brown needles, m. p. 244°; *acid hydrochloride*, yellow, crystalline precipitate, which decomposes at about 140°). Demethylation of the *pseudo*-base with concentrated hydrochloric acid at 160—170° gives *2:6-diphenyl-4-*p*-hydroxyphenylpyrylium hydrochloride*, steel-blue, shining needles, m. p. 320°, after slowly changing from 235° (an *acid chloride*, $C_{23}H_{17}O_2Cl,0{\cdot}5HCl$, yellow crystals, is also described); demethylation with hydrobromic acid gives the corresponding *bromide*, brownish-red crystals, m. p. above 320°, which appears to exhibit little tendency towards further combination with the halogen acid. The chloride is converted by water and a slight excess of sodium acetate into 2:6-diphenyl-4-quinopyran, O<(CPh:CH)(CPh:CH)>C:C_6H_4:O, dark red crystals with a bronze glance, m. p. 262—264°; the anhydro-base is almost instantaneously decolorised by semicarbazide, but does not yield a semicarbazone. Addition of water to the anhydro-base occurs less readily than with the α-isomeride, and is best effected by cautious addition of water to the alcoholic solution, whereby the *carbinol* base, O<(CPh:CH)(CPh:CH)>C<(OH)(C_6H_4·OH), is precipitated in pale red crystals. It is much less stable than the corresponding α-derivative, and

readily loses water when heated, and re-forms the pseudo-bas It is more readily isolated as its *monoacetyl* derivative, pale yellov silky needles, m. p. 122—123°.

Prolonged action of pyridine on the demethylated chloride lead to the *formation of two substances*, $C_{23}H_{20}O_4$, needles, m. p. 166 and $C_{23}H_{20}O_6$, colourless crystals, m. p. 239—240°, respectivel These compounds do not exhibit any relationship to the re anhydro-base, and are probably formed by fission of the ring.

[*Addendum to Part IV*.—W. DILTHEY.]—The *disemicarbazone* o α-hydroxy-ε-keto-γε-diphenyl-α-p-hydroxyphenyl-$\Delta^{\alpha\gamma}$-pentadien forms colourless, transparent prisms, m. p. 191—192°. The aci picrate of 2:6-diphenyl-4-*p*-anisylpyrylium, m. p. 237—238° (A. 1919, i, 413) is now found to have a normal constitution. H. W.

Pyrylium Compounds. VII. Carbonium or Oxonium? WALTHER DILTHEY (*Ber.*, 1920, **53**, [*B*], 261—265).—The author i led to reject the carbonium formula for pyrylium compounds, sinc several basic carbon atoms must be taken into consideration, an thus there is no possibility of a uniform conception. For a simila reason, the oxonium formula is rejected. Regarding the basic pro perties of oxygen as proved, there would be in the pyrylium salt three carbon atoms and two oxygen atoms to which negative radicle might be attached, whilst it is also possible that the para-carbo atom of the phenyl residue can function in the formation of salts In proportion as the number of basic atoms in the molecul increases, it becomes more certain that no single one of them i united to the negative group, and more probable that the latte is attached to the molecule as a whole. A somewhat similar ide has been advanced by Kauffmann (this vol., i, 50), who, howeve regards the cationic partial valencies as associated with definit atoms. It appears simpler to the author to regard the complex a a whole rather than the individual atoms as carriers of the electron Adopting these ideas, the annexed formula is proposed for th pyrylium salts, which represents the negativ group as freely mobile in the "second" zone and attached to no particular atom, but to th total complex. The fourth carbon valencie are disposed in such a manner as to indicat that one of them resembles the carbon ator of triphenylmethyl, and to express the possibility of the return o the hydroxyl group in the formation of pseudo-bases to either th α- or the γ-carbon atom. When this has occurred, the remainin valencies arrange themselves to ordinary double bonds; it is als shown that the β-carbon atoms cannot combine with the hydroxyl Since this conception can readily be expanded to triphenylmethy and to the nitrogen atoms of azines, oxazines, and thiazines, a uniform conception of a large class of dye-salts is secured.



H. W.

Syntheses of Methylenecoumarins. L. CLAISEN (*Ber.*, 1920, **3**, [*B*], 322—325).—In a recent communication (A., 1919, i, 340), dams and Rindfuss have described the action of bromine on cetylated *o*-allylphenols and the elimination of the bromine from ie product by boiling alcoholic potassium hydroxide, whereby they btain substances which they consider to be methylenecoumarans the type $C_6H_4<{CH_2 \atop O}>C:CH_2$. The author points out that he as used this process previously (A., 1913, i, 1175; 1919, i, 266), nd that it yields coumarones of the type $C_6H_4<{CH \atop O}>CMe$. Vhilst agreeing with Adams and Rindfuss that the compound $_6H_4<{CH_2 \atop O}>CH\cdot CH_2Br$ is formed as an intermediate stage, he oes not consider that the further elimination of hydrogen bromide ust of necessity cause the final production of a substance with ie double bond in the side-chain, since, under the experimental onditions, one of the two bonds would almost certainly pass to ie nucleus. Further, the observation of Adams and Rindfuss iat their "methylenecoumaran" yields a monobromo-derivative om which bromine cannot be removed by alcoholic potassium ydroxide or silver nitrate, is most readily explained on the ssumption that it is a methylcoumaran brominated in the nucleus.

H. W.

4′-Methoxy-1′-naphthyl-2-chromone. S. RUHEMANN and I. LEVY (*Ber.*, 1920, **53**, [*B*], 265—274).—4-Methoxy-1-naphthdehyde, b. p. 200—202°/10 mm., is converted by ethyl acetate nd metallic sodium into *ethyl β-4-methoxy-1-naphthylacrylate*, $Me\cdot C_{10}H_6\cdot CH:CH\cdot CO_2Et$, yellow prisms, m. p. 59°, which is adily hydrolysed to the corresponding acid, m. p. 215° (compare ousset, A., 1899, i. 296; Windaus and Bernthsen-Buchner, A., 917, i, 670). The latter is reduced by sodium amalgam to 4-methoxynaphthylpropionic acid, colourless needles, m. p. 63—164° (Windaus and Bernthsen-Buchner, *loc. cit.*, give 65—166°), the *silver* salt and *ethyl* ester, colourless oil, b. p. 06—207°/10 mm., of which are described. Attempts to convert ie acid into a hydrindone by means of phosphorus pentachloride nd aluminium chloride were unsuccessful, the product being an oil, hich did not crystallise and could not be distilled without decomosition.

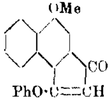
Ethyl αβ-dibromo-β-4-methoxy-1-naphthylpropionate,

$$OMe\cdot C_{10}H_6\cdot CHBr\cdot CHBr\cdot CO_2Et,$$

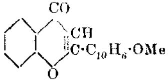
olourless needles, m. p. 108—109° (decomp.), is obtained in quantiitive yield from the unsaturated ester and bromine in carbon sulphide solution. It is a somewhat unstable substance, which adily decomposes when gently warmed; it is converted by coholic potassium hydroxide solution into *4-methoxy-1-naphthylropiolic acid*, yellow needles, m. p. 159° (decomp.), from which

4-methoxy-1-naphthyl methyl ketone, colourless prisms, m. p. 72—73°, is prepared by prolonged treatment with boiling water. Methoxynaphthylpropiolic acid cannot be esterified in the usual manner; thus, treatment with boiling 2—3% alcoholic hydrogen chloride converts it into *ethyl β-chloro-4-methoxy-1-naphthylacrylate*, $OMe\cdot C_{10}H_6\cdot CCl\colon CH\cdot CO_2Et$, yellow, viscous oil, b. p. 230—240°/15 mm. (partial decomp.). *Methyl 4-methoxy-1-naphthylpropiolate*, colourless needles, m. p. 97°, is prepared from the acid, methyl sulphate, and potassium hydroxide, whilst the *ethyl* ester, yellow prisms, m. p. 81—82°, is similarly obtained, but in very poor yield, with the aid of ethyl iodide.

Ethyl β-phenoxy-β-4-methoxy-1-naphthylacrylate is prepared as a viscous, red oil, which did not show any tendency to crystallise, and which was not further purified by the action of sodium phenoxide on ethyl β-chloro-β-4-methoxy-1-naphthylacrylate; it was hydrolysed by methyl-alcoholic potassium hydroxide to a mixture of the corresponding *acid*, brown prisms, m. p. 180—181° (decomp.), and the *phenyl ether of 3-hydroxy-8-methoxy-αβ-naphthind-1-one* (I), colourless prisms, m. p. 186—187°.



(I.)

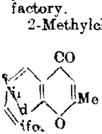


(II.)

Successive treatment of β-phenoxy-β-4-methoxy-1-naphthylacrylic acid with phosphorus pentachloride and aluminium chloride yields *4′-methoxy-1′-naphthyl-2-chromone* (II), pale yellow needles, m. p. 177—178°. H. W.

Formation of Chromones. S. Ruhemann (*Ber.*, 1920, **53**, [*B*], 285—287).—The methods available for the synthesis of chromones (Ruhemann, T., 1900, **77**, 1184; 1901, **79**, 470, 918, 1185; 1902, **81**, 419; Simonis and Rennert, A., 1914, i, 980) suffer under the disadvantage that the yields are very small. The author has therefore endeavoured to synthesise these substances from ethyl β-chlorocrotonate, using a procedure which, in the aromatic series, readily yielded the flavones; although preparation can be effected in this manner, the yields are unsatisfactory.

2-Methylchromone (annexed formula), colourless needles, m. p. 72—73°, is obtained by the successive action of phosphorus pentachloride and aluminium chloride on β-phenoxycrotonic acid. Similarly, *β-p-tolyloxycrotonic acid*, colourless needles, which gradually decompose when heated, softening at 145° and becoming completely molten at about 159—160° (*ethyl* ester, colourless oil, b. p. 152—153°/14 mm.), is transformed into *2:6-dimethylchromone*, colourless prisms, m. p. ..°; the latter, like other chromones (Ruhemann, T., 1902,



81, 419), yields a *platinichloride*, $(C_{11}H_{10}O_2)_2,H_2PtCl_6$, orange prisms, which darken when heated and have m. p. 185° (decomp.).

H. W.

The Parent Substance of Adrenaline. KARL W. ROSENMUND and H. DORNSAFT (*Ber.*, 1920, **53**, [*B*], 317—318. Compare this vol., i, 56).—In reply to the criticism of Knoop (this vol., i, 161), the authors point out (i) that adrenaline is produced in such small quantity in the organism that it is probable that the main processes of degradation of amino-acids are not concerned with its formation, and (ii) that the sequence of changes of amino-acids which they have postulated is not hypothetical, but is based on changes which have been established experimentally for micro-organisms.

H. W.

The Identity of Aribine with Harman. ERNST SPÄTH (*Monatsh.*, 1919, **40**, 351—359).—The fact that aribine can be sublimed without decomposition is difficult to reconcile with the molecular weight required by Rieth's formula, $C_{23}H_{20}N_4$ (*Annalen*, 1861, **120**, 247). A comparison of the alkaloid with harman, $C_{12}H_{10}N_2$ (Fischer, A., 1901, i, 405), revealed the complete identity of the bases (m. p. 237—238° in a vacuum), of their hydrochlorides (each showing intense blue fluorescence in acid solution), of their aurichlorides (darkening in a vacuum at 207° and melting at 211—213° [decomp.]), of their platinichlorides (straw-yellow needles, which turn brown in a vacuum at 255—260°, and are not melted at 280°), and of their picrates (yellow crystals, which become brown in a vacuum at 215°, dark brown at 240°, and black at 250—255°).

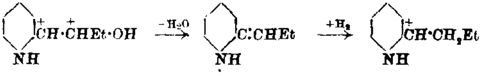
J. K.

Some New Compounds of Caffeine and Theobromine, Soluble in Water. J. ABELIN (*Apoth. Zeit.*, **34**, 316; from *Chem. Zentr.*, 1919, iii, 957).—The alkali and alkaline-earth salts of aromatic carboxylic acids and of all ω-methylsulphonic acids of carbo- and hetero-cyclic amines yield complex compounds with caffeine and theobromine which are freely soluble in water and, in part, are of therapeutic value. Since aqueous solutions of *o*-acetoxybenzoic acid are readily decomposed, with elimination of acetic acid when slightly warmed, the preparation of *calcium caffeine-o-acetoxybenzoate* is effected by suspending calcium *o*-acetoxybenzoate (100 grams) in anhydrous alcohol or acetone (500 c.c.), and, with continuous stirring, adding a solution of caffeine (55 grams) in chloroform; the solvent is subsequently allowed to evaporate at a low temperature. The purity of the product is tested by treating its aqueous solution with ferric chloride, which should yield a coffee-brown precipitate, but not a violet coloration (absence of salicylic acid). *Calcium theophylline-o-acetoxybenzoate* is similarly prepared from solutions of theophylline in pyridine or benzyl alcohol. The caffeine and theophylline *compounds* of the ω-methyl-

sulphonates of the amines are prepared by mixing solutions o equimolecular quantities of the components in water and evapor ating the solutions on the water-bath at a low temperature, or if the amine salt is insufficiently stable to withstand this treat ment, a solution of caffeine in chloroform is added to a suspensio of the sodium salts of the ω-methylsulphonic acids of *p*-phenetidin (*neraltine*), of *4-aminoantipyrine* (melabrin), of aniline, *p*-toluidine or naphthylamine in alcohol, acetone, or chloroform, and the solvent is removed with continuous stirring at a gentle temperature.

H. W.

The Ability of Plants to Form Optical Antipodes. KUR HESS and WILHELM WELTZIEN (*Ber.*, 1920, **53**, [*B*], 119—129).— The normal products of animal metabolism occur in optically activ forms and never in their possible antipodes; an apparent exceptio to this rule is found in the production of optically inactive lacti acid by the fermentation of dextrose, but in this case it has bee established that methylglyoxal is an intermediate product, fron which, by an intramolecular Cannizzaro reaction, the lactic acid i finally formed, that is, the final stage is not an enzymic proces In the case of the plant organism, on the other hand, optical anti podes are not infrequently produced simultaneously; examples o this are coniine and methylconiine in *Conium maculatum*, pelle tierine, *iso*pelletierine and methyl*iso*pelletierine, atropine laudanine, scopoline, paricine, cryptopine, arabine, cevadine delphinine, and delphinoidine. The production of optically in active bases which contain at least one asymmetric carbon may b ascribed to one of the following causes: (i) racemisation may hav occurred during the treatment of the plant with extracting solvents (ii) racemisation of a primarily formed optically active alkaloi may have occurred within the plant during its life, and (iii) form ation of the alkaloid may be brought about by "symmetrical" processes, either by symmetrical enzymes or by total or partia processes in which enzymes do not play a part. Thus, coniine ma possibly be formed in the following manner:



which would be analogous to the production of *dl*-lactic acid from dextrose, with intermediate formation of methylglyoxal. The possibility indicated in (i) may be exemplified by atropine, since *l*-hyoscyamine is readily racemised by dilute alkali at the ordinary temperature and by preservation of its alcoholic solution, whilst protracted treatment with potassium carbonate solution is used in extracting the alkaloid from *Atropa belladonna*. Pelletierine and the allied substances have been shown to be readily racemised, but not under conditions such as are observed in their extraction, whilst

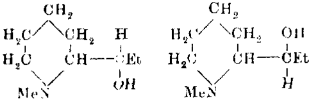
also, no activity is observed in the fresh extracts. *d*-Coniine and *l*-methylconiine are racemised with such difficulty that it is impossible to assume that racemisation occurs in the process of extraction or within the living plant. The case of scopoline is somewhat different, and it appears impossible to attribute the optical inactivity of the natural product to any of the three causes above-mentioned, since King (T., 1919, **115**, 476, 974) has shown that the active base is by no means readily racemised, and an explanation on the lines of that given for *dl*-lactic acid is out of the question. There would thus appear to be an example of a fundamentally different mode of action in the animal and the plant organism.

[In part with (FRL.) H. KAULLA.]—Coniine is not racemised when heated with concentrated hydrochloric acid during 104 hours at about 200° (compare Hess and Eichel, A., 1918, i, 34). Similarly, *d*-methylconiine is unchanged by similar treatment during 120 hours, by the action of ethyl-alcoholic sodium ethoxide solution during 12 hours at 200°, or of aqueous ethyl-alcoholic sodium solution under the same conditions, or by boiling alcoholic potassium hydroxide solution during 45 hours. H. W.

The Asymmetric, Tervalent Nitrogen Atom. III. Methyldihydro*iso*pelletierine and *dl*-Methylconhydrine [Methyldihydroconhydrinone]. KURT HESS (*Ber.*, 1920, **53**, [*B*], 129—139).—In previous communications (A., 1919, i, 345; this vol., i, 86) it has been shown that methyl*iso*pelletierine and *dl*-methylconhydrinone are structurally identical, racemic compounds, the isomerism of which can only be explained by the assumption of a second asymmetric centre in addition to the asymmetric carbon atom, which can only be the tervalent nitrogen atom. Since each compound is oxidised to piperidine-2-carboxylic acid and reduced to *dl*-methylconiine, it appeared that the stereoisomerism was in some manner conditioned by the presence of the carbonyl group. It is now found, however, that the four amino-alcohols obtained by reduction of methyl*iso*pelletierine and *dl*-methylconhydrinone are all different, so that the isomerism of the parent substances persists in the corresponding alcohols. The carbonyl group of the ketones cannot therefore have the importance which was previously attributed to it, and the cause of the isomerism is to be sought in the arrangement of the groups around the nitrogen atom. If, however, the oxygen atom is entirely removed, the isomerism disappears. It may be further noted that the methiodides of the hydramines of both series are different, and afford a rather unusual example of asymmetric arrangement in a compound of the type N(AABC)X; a similar instance has been observed by Freund and Kessler (A., 1919, i, 283) in the quinoline series.

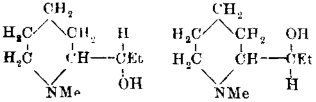
Methyl*iso*pelletierine is readily reduced by sodium amalgam and water at the ordinary temperature to a mixture of *a-methyldihydroisopelletierine*, b. p. 101—106°/15 mm., and slightly impure

β-methyldihydroisopelletierine, b. p. 115—120°/15 mm. (annexed formulæ), which are separated by fractional distillation. The α-base does not yield crystalline salts with the halogen acids or with chloroplatinic acid, but gives a crystalline methiodide, m. p. 176°, an oily *picrate*, and an oily m-*nitrobenzoyl* derivative, b. p. ca. 220°/17 mm. The β-base gives a *methiodide*, cubes, m. p. 176—177°, a *picrate*, prisms, m. p. 123—124°, and an oily m-*nitrobenzoyl* derivative, which could not be distilled without almost complete decomposition. Reduction of either base by phosphorus and hydriodic acid at 125—135° gave *dl*-methylconiine, identified as the platinichloride and aurichloride.



α-Base. β-Base.

α-dl-*Methylconhydrine*, b. p. 97—99°/16 mm., and β-dl-*methylconhydrine*, b. p. 91—101°/15 mm. (annexed formulæ), are obtained by the action of formaldehyde and formic acid on the corresponding hydramines. The α-base gives a *methiodide*, prisms, m. p. 178—179°, a *picrate* (+0·5EtOH), rods, m. p. 79—80°, and an oily m-*nitrobenzoyl* derivative. The *methiodide* of the β-base crystallises in prisms, m. p. 174°, the *picrate* forms irregular plates and cubes, m. p. 133—134°, and the m-*nitrobenzoyl* derivative is an oil. Reduction of either base by hydriodic acid and red phosphorus yields *dl*-methylconiine.



α-Base. β-Base.

Isomerism of the amino-alcohols is not so sharply marked as that of the ketones, since in the former case the m. p.'s of the salts are nearly identical, whilst in the latter case they differ by 30—40°; the individuality of the salt is, however, readily demonstrated by the mixed melting-point method. H. W.

The Asymmetric, Tervalent Nitrogen Atom. IV. Non-existence of Ladenburg's *iso*Coniine. KURT HESS and WILHELM WELTZIEN (*Ber.*, 1920, **53**, [*B*], 139—149).—Some years ago Ladenburg (A., 1906, i. 692, and previous abstracts) described the preparation of *iso*coniine, and explained its isomerism with coniine by the hypothesis of an asymmetric, tervalent nitrogen atom. On theoretical grounds, the authors have been led to doubt the existence of this instance, since the salts of coniine and *iso*coniine have identical melting points, which is unusual in a case of this kind, whilst, secondly, *dl*-methylconiine (preceding abstract) is incapable

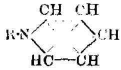
of existence in the corresponding isomeric forms, and the same is therefore probably true for coniine itself, and, thirdly, *l*-coniine has been synthesised by Löffler (A., 1909, i, 180) and found to be identical with the natural substance. They have therefore repeated Ladenburg's work, and obtained results which are practically identical with his. The possibility that *iso*coniine as prepared in this maner is contaminated with an impurity which affects the specific rotation, but is eliminated in the purification of the salts, has been examined by adopting a different mode of synthesis, which is found to yield a material identical in all respects with natural *d*-coniine. The higher optical activity of Ladenburg's synthetic coniine preparation is therefore to be attributed to the presence of impurities, and *iso*coniine is to be deleted from the literature

Ladenburg's synthesis has been slightly modified. Methyl-α-picolylalkine is reduced by phosphorus and hydriodic acid, but as the product is found to contain about 65% of 2-allylpyridine, the conversion to the propyl derivative is completed by means of hydrogen in the presence of platinum. The *dl*-coniine is prepared by reduction of 2-propylpyridine by sodium and alcohol, and is resolved by *d*-tartaric acid. The hydrogen tartrate and platinichlorides of the synthetic and natural bases appeared identical in all respects, but the synthetic base had $[\alpha]_D + 19{\cdot}01°$, whereas the natural product had only $[\alpha]_D + 15{\cdot}21°$.

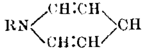
The preparation of *dl*-coniine from methyl α-picolylalkine has been effected in a somewhat different manner, in that the substance is first converted into the piperidine derivative by hydrogen in the presence of platinum, and the hydroxy-group is subsequently reduced by treatment with phosphorus and hydriodic acid, followed by zinc and sulphuric acid; in this manner, the formation of an allyl derivative is avoided. The racemic base is resolved by *d*-tartaric acid; the specific rotation of the hydrogen tartrate is $+20{\cdot}06°$ in alcoholic solution, whilst the base obtained from it has $[\alpha]_D^{17} + 14{\cdot}96°$, which agrees well with the specific rotation of the natural product. H. W.

A Radicle with Quadrivalent Nitrogen. BRUNO EMMERT (*Ber.*, 1920, **53**, [*B*], 370—377).—Dimethyl- or diethyl-tetrahydrodipyridyl, $R{\cdot}N{<}{\substack{CH:CH \\ CH:CH}}{>}CH{\cdot}CH{<}{\substack{CH:CH \\ CH:CH}}{>}N{\cdot}R$ (Hofmann, A., 1881, 921; Emmert, A., 1909, i, 602; 1917, i, 221; 1919, i, 455), is soluble in alcohol, yielding a yellowish-brown solution, which slowly at the ordinary temperature, but more rapidly when warmed, becomes deep blue; the blue coloration disappears immediately when the solution is shaken with air, but slowly reappears, and can be again removed until a molecule of oxygen has been absorbed for each molecule of substance. The phenomena are thus analogous with those observed by Schmidlin (A., 1908, i, 623) in the case of triphenylmethyl. In the present instance, there is the possibility

of the formation of two radicles (annexed formulæ, I and II) containing, respectively, a quadrivalent nitrogen or a tervalent carbon atom, which on oxidation should yield a pyridinium hydroxide or a peroxide; actually, the formation of methylpyridinium hydroxide from dimethyltetrahydrodipyridyl (identified as the chloride and platinichloride) is established. In the case of benzyltetrahydrodipyridyl, the blue coloration of the alcoholic solution is only developed on warming. Solutions in ether are yellow, and do not become blue. Solutions in chloroform are intermediate in their properties between those in ether and alcohol; the yellow solution, when preserved with exclusion of air, slowly becomes pale green to bluish-green, which may be regarded as a mixture of the yellow and blue colorations. The following experiments show that the blue solutions actually contain the radicle (I); the alcoholic solutions are instantaneously decolorised by iodine and yield *N-alkylpyridinium iodides*, as is shown by the isolation of these substances and by the estimation of ionisable iodine in the crude products. Addition of iodine to the yellow, ethereal solutions causes partial resinification; allylpyridinium iodides are also formed in small amount, together with larger quantities of yellow, amorphous powders, which could not be further purified, but which are shown to contain an atom of iodine for each pyridine nucleus. A mixture of alkylpyridinium iodide and the yellow, amorphous iodo-compound is formed from the chloroform solution.



(I.)



(II.)

In the case of triphenylmethyl, the degree of dissociation, and consequently the intensity of colour of the solution, diminishes with decreasing temperature. The blue, alcoholic solutions of the dialkyltetrahydrodipyridyls become violet-red at $-80°$, whilst that of the dibenzyl derivative changes to brown, the colour in each case being restored when the solution is warmed; the reason of the non-disappearance of the colour has not been elucidated.

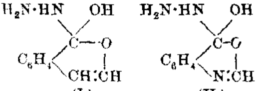
The tendency of the dialkyltetrahydrodipyridyls to dissociate into radicles is ascribed to the weakening of the valency uniting the γ-carbon atoms by the demands of the numerous double bonds, and cannot be ascribed to steric hindrance, which has been so frequently advanced as a theory in the triphenylmethyl series. H. W.

The Action of Ethyl Chloroformate on Pyridine and Quinoline. THOMAS HOPKINS (T., 1920, **117**, 278—282).

Crystallographic Properties of a Compound $C_{11}H_9O_2N$. JOHNSEN (*Centr. Min.*, 1919, 33—34).—The compound, which possibly has the structure $CHPh:C<\begin{matrix}CO-CO\\NH\cdot CH_2\end{matrix}$, melts at ...0·5° (decomp.), and crystallises from benzene in short ...s with indistinct end faces; $a:b:c = 1·335:1:0·57$;

$\beta = 114°18\frac{1}{2}'$. D^{16} 1·345. Cleavages were observed parallel to the faces {100} and {101}. The optic axial angle is large, and n_β 1·756. E. H. R.

Constitution of Acylanthranilic Anhydrides. G. Schroeter (*Ber.*, 1920, **53**, [*B*], 230—232).—In a recent communication (this vol., i, 181), Heller and Lauth have described the preparation of hydrazino-derivatives of simple and complex acylanthranyls, to which they have attributed the general structure $\begin{matrix}CO\\C_6H_4\end{matrix}\!\!>\!N{\cdot}COR$ instead of $C_6H_4<\begin{matrix}CO{\cdot}O\\N{=}C{\cdot}R\end{matrix}$. The author, however, regards the formation of the hydrazine additive products as additional evidence in favour of the lactonic formulæ; he points out, for example, that the anhydride of formylanthranilic acid may be regarded as *iso*coumarin, in which a CH group is replaced by nitrogen, and that, therefore, their hydrazino-compounds may be similarly formulated (annexed formulæ, I and II). The lactone formula further explains why acylanthranilic acids which contain the group ·NH·CO· readily form unimolecular anhydrides, owing to preliminary change into the desmotropic form ·N:C(OH)·, whereas those in which this desmotropic change is structurally impossible give bimolecular anhydrides. H. W.


(I.) (II.)

Products of the Action of Oxalyl Chloride on Acid Anilides. R. Stollé and M. Luther (*Ber.*, 1920, **53**, [*B*], 314—317).—When acetanilide is heated with rather more than a molecular proportion of oxalyl chloride in carbon disulphide solution, it yields a *compound*, $C_{10}H_7O_3N$, m. p. 143° (not quite definite), which, mainly by reason of the readiness with which it is decomposed by water into acetic and oxanilic acids, is regarded as 4:5-diketo-3-phenyl-2-methylenetetrahydro-oxazole, $O<\begin{matrix}C(:CH_2)\\CO{-}CO\end{matrix}>NPh$. When warmed with alcohol, it gives *4:5-diketo-2-ethoxy-3-phenyl-2-methyltetrahydro-oxazole*, colourless needles, m. p. 98°. Under similar conditions, diethylacetanilide and oxalyl chloride (1:1) give *4:5-diketo-3-phenyl-2-diethylmethylenetetrahydro-oxazole*, m. p. 69°.

The compounds obtained by Figée (A., 1915, i, 869) from molar quantities of oxalyl chloride and propionanilide or phenylacetanilide are to be regarded as 4:5-diketo-3-phenyl-2-ethylidenetetrahydro-oxazole and 4:5-diketo-3-phenyl-2-benzylidenetetrahydro-oxazole. H. W.

Preparation of Octanitrodiphenylethylenediamine. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 300082; from *Chem. Zentr.*, 1920, ii, 188).—*Octanitrodiphenylethylenediamine*.

$C_6H_2(NO_2)_3 \cdot N(NO_2) \cdot CH_2 \cdot CH_2 \cdot N(NO_2) \cdot C_6H_2(NO_2)_3$, is prepared by the action of concentrated nitric acid on 2:4:2′:4′-tetranitrodiphenylethylenediamine or 2:4:6:2′:4′:6′-hexanitrodiphenylethylenediamine; it crystallises from concentrated nitric acid in colourless, rhombic prisms, m. p. 213° (violent decomp.), and is almost insoluble in the usual organic media. It is an extremely sensitive explosive. H. W.

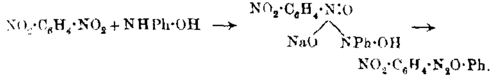
Absorptive Power of Uric Acid towards Dyes. ALBE BENOIT (*Compt. rend. soc. biol.*, 1919, **82**, 1051—1052; from *Chem. Zentr.*, 1920, i, 168).—Uric acid has the power of adsorbing precipitated colloids from their solutions. If methylene-blue is administered to a subject who separates uric acid freely, the sediment is coloured blue. If a trace of dye is added to a hot saturated solution of uric acid, coloured crystals of the latter are deposited from the cold solution. When a cold saturated solution of a normal urate is treated with a small quantity of a soluble dye and then acidified with a trace of hydrochloric acid, the precipitated uric acid adsorbs the dye, and can even cause complete decolorisation of the solution. H. W.

State of Uric Acid in Solution. ALBE BENOIT (*Compt. rend soc. biol.*, 1919, **82**, 1052—1053; from *Chem. Zentr.*, 1920, i, 168) —Uric acid may be present in solution in two physically different conditions, in one of which it is stable, flocculent, and crystalline and cannot adsorb dyes, whilst in the other it is metastable; it i found in the latter condition in supersaturated solution in urine Uric acid is therefore probably more soluble in colloidal solution than in the corresponding quantity of distilled water at the sam temperature. H. W.

Action of *N*-Phenylhydroxylamine on Aromatic Nitro compounds. JAKOB MEISENHEIMER (*Ber.*, 1920, **53**, [B] 358—369).—The action of hydroxylamine on *m*-di- and tri-nitro compounds leads to the substitution of hydrogen atoms attache to the nucleus by amino-groups, whereas with *o*- and *p*-dinitroaryl reduction to the corresponding dihydro-derivatives occurs (Meisenheimer and Patzig, A., 1906, i, 642, 652). It is now shown tha the reaction with phenylhydroxylamine follows a similar course i each case.

[With IVAN SMOLNIKOV.]—When *m*-dinitrobenzene and pheny hydroxylamine react in methyl-alcoholic solution in the presence of potassium hydroxide, a mixture of azoxybenzene, α-3-*nitro-azoxybenzene*, yellow needles, m. p. 120—121°, and β-3-*nitro-azoxybenzene*, pale yellow needles, m. p. 86—88°, is obtained. Th latter substances are reduced by ammonium sulphide to 3-*nitro-1-hydrazobenzene*, yellow crystals, m. p. 84—85°, which is oxidise by mercuric oxide to 3-nitro-1-azobenzene, m. p. 95—96° (compar

Bamberger and Hübner, A., 1904, i, 117). The course of the *condensation* is indicated by the scheme:



A similar mixture of azoxy-compounds is obtained from 1:3:5-trinitrobenzene, but in this instance only the more sparingly soluble 3:5-*dinitro*-1-*azoxybenzene*, practically colourless crystals, m. p. 170—171°, was isolated.

2:4-Dinitrotoluene yields with azoxybenzene, *a-benzeneazoxy-2-nitro-*p*-toluene*, yellow crystals, m. p. 123—124°, *β-benzeneazoxy-2-nitro-*p*-toluene*, m. p. 119—120°, and a substance, m. p. 160°, which is very probably 2:2′-dinitro-4:4′-azoxytoluene. Reduction of the benzeneazoxynitrotoluene yields the corresponding *hydrazobenzene*, which, without being isolated, was oxidised to *benzeneazo-2-nitro-*p*-toluene*, orange-red needles, m. p. 103—104°, the constitution of which is established by its synthesis from nitrosobenzene and 3-nitro-*p*-toluidine.

The nitro-group appears capable of adding hydroxylamine in the manner described above only if both the ortho-positions with respect to it are free. Thus 2:6-dinitrotoluene is converted into 2:2′-dinitro-6:6′-azoxytoluene, nearly colourless crystals, m. p. 189—190° (Brand and Zoller, A., 1907, i, 755).

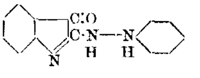
The additive power of nitro-groups in the *m*-, di-, and tri-nitro-compounds is greatly influenced by the presence of other substituents; preliminary experiments show that 2:4:6-trinitrotoluene and 2:4:6-trinitrophenetole react in a quite different manner (which has not been further examined), whilst 2:4:6-trinitro-*m*-xylene remains nnaffected.

When 1:3:5-trinitrobenzene and phenylhydroxylamine are dissolved in alcohol, a crystalline *substance* is slowly deposited (pale yellow leaflets or needles, m. p. 123—124°), which is formed from 1:3:5-trinitrobenzene (2 molecules) and azoxybenzene (1 molecule), the latter being obviously formed by the auto-decomposition of phenylhydroxylamine. *m*-Dinitrobenzene behaves similarly, yielding m-*dinitrobenzeneazoxybenzene*, $C_{18}H_{14}O_5N_4$, yellow plates, m. p. 52—54°. Azoxybenzene was also found to give additive *products* with 1:3:5-trinitrobenzene, with 2:4:6-trinitrotoluene (yellow leaflets, m. p. 64—66°), and with *m*-dinitrobenzene, but not with 2:4:6-trinitrophenetole or 2:4-dinitrotoluene. Azobenzene was less reactive, but yielded an additive *compound* with trinitrobenzene (compare Hofmann and Kirmreuther, A., 1910, i, 548), but not with 2:4:6-trinitrotoluene, 2:4:6-trinitrophenetole, *m*-dinitrobenzene, or 2:4-dinitrotolnene. H. W.

Azo-derivatives of Indoxyl. J. Martinet and O. Dornier (*Compt. rend.*, 1920, **170**, 592—594).—Azo-derivatives of indoxyl

may readily be prepared by adding to a mixture of ice and indoxyl neutralised with sulphuric acid, the requisite amount of a diazo-compound. In this way the authors have prepared: o-*Tolueneazoindoxyl*, m. p. 249° (decomp.). m-*Tolueneazoindoxyl*, m. p. 232° (decomp.). p-*Tolueneazoindoxyl*, m. p. 256° (decomp.). m-4-*Xyleneazoindoxyl*, m. p. 244° (decomp.). *ψ-Cumeneazoindoxyl*, m. p. 245° (decomp.). *α-Naphthaleneazoindoxyl*, m. p. 202° (decomp.). *β-Naphthaleneazoindoxyl*, m. p. 220° (decomp.).

All the m. p.'s given are approximate owing to decomposition.



Benzeneazoindoxyl, when reduced in alkaline solution by sodium hyposulphite, gives aniline, ammonia, and indirubin.

The authors discuss the structure of these azo-compounds, and suggest as a possible constitution the formula annexed as an alternative to that supported by Baeyer (compare A., 1884, 74) and Heumann (compare *Ber.*, 1893, **26**, 226) or the one supported by Heller (compare A., 1907, i, 442). W. G.

Diazo-compounds. Thermochemical Investigations. W. Swientoslawski (*Ann. Soc. d'Encour. Sci. Expt.*, 1917, Suppl. No. 7. Reprint 15 pp.).—In part a very brief résumé of work already published (compare A., 1909, ii, 547, 864; 1910, ii, 588, 691; 1911, ii, 188, 967; 1914, ii, 105, 107; 1918, ii, 32).

The author has measured the heat of reaction of varying proportions of sodium hydroxide on different oximes aud of excess of hydrochloric acid on the same oximes, and on these results bases a discussion of the constitution of the oximes and their relationship to the diazonium hydroxides. The heats of reaction indicate that α-benzaldoxime is more strongly acid than β-benzaldoxime, and in this respect closely resembles acetaldoxime. Accordingly, for the two oximes the following structures are suggested:

β-.	α-.
Ph·C·H ‖ N·OH	Ph·C·H ‖ HO·N

and from these the structures of the diazo-compounds are deduced as follows, the *iso*-form being more acid than the normal form:

Normal.	*iso*.
Ph·N ‖ N·OH	Ph·N ‖ HO·N

Finally the author puts forward the hypothesis that in certain compounds containing nitrogen the atom (or atoms) undergo a deformation, the three valencies of nitrogen being displaced, and the atom loses one of its planes of symmetry. This deformation is accompanied by an increase of acidity. Thus there is:

$\begin{matrix}R\\H\end{matrix}>C{:}NOH$	R·N:N·OH
Unstable form of aldoxime.	Normal diazonium hydroxide.
$\begin{matrix}R{\cdot}C{\cdot}H\\ \vert\\ HO{\cdot}\mathbf{N}\end{matrix}$	$\begin{matrix}R{\cdot}\mathbf{N}\\ \Vert\\ HO{\cdot}\mathbf{N}\end{matrix}$
Stable form of aldoxime.	*iso*Diazonium hydroxide.

the nitrogen atom indicated by **N** having undergone deformation.

In a final chapter the author discusses the relative merits of Cain's and Blomstrand's structural formulæ for diazo-compounds, and quotes certain facts which, in his opinion, are opposed to Cain's formula. At the same time he considers that Blomstrand's formula does not offer an explanation of all the known properties of the diazo-compounds. W. G.

Condensation Products from *p*-Aminoazobenzene and Ketones or Aldehydes. G. Reddelien (*Ber.*, 1920, **53**, [*B*], 340—344).—Benzophenone is scarcely affected by being heated with *p*-aminoazobenzene even after addition of hydrobromic acid (compare this vol., i, 315); reaction, however, occurs readily if benzophenoneanil (A., 1913, i, 1203) is substituted for the ketone, the necessary condition consisting in the removal of the liberated aniline, which is readily effected by performing the operation in a vacuum at 180°; the p-*diphenylmethyleneaminoazobenzene*, $CPh_2{:}N{\cdot}C_6H_4{\cdot}N_2{\cdot}Ph$, forms coarse, orange-yellow crystals, or, less frequently, large, less intensely coloured plates, both varieties having m. p. 123°. It yields an orange-red *monohydrochloride* and a dark red *dihydrochloride*, both of which are rapidly decomposed by traces of moisture into aminoazobenzene hydrochloride and benzophenone. p-*Fluorenylideneaminoazobenzene*, long, orange-yellow, strongly dichroic needles, m. p. 141—142°, is prepared similarly.

For comparative purposes, the following condensation products of aldehydes and *p*-aminoazobenzene have been prepared: p-*cinnamylideneaminoazobenzene*, $CHPh{:}CH{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}N_2{\cdot}Ph$, orange-yellow leaflets, m. p. 137—138° (*hydrochloride*, orange-red, crystalline powder); p-*dimethylaminobenzylideneaminoazobenzene*, orange-yellow crystals, m. p. 174—175°; *di*-p-*dimethylaminophenylmethyleneaminoazobenzene* $(NMe_2{\cdot}C_6H_4)_2C{:}N{\cdot}C_6H_4{\cdot}N_2{\cdot}Ph$, orange-red needles, m. p. 232—233°. The halochromic phenomena on solution in concentrated sulphuric acid are shown in the following table:

	Colour of substance.	Colour of solution.
Benzylideneaminoazobenzene...........	orange-yellow.	orange-red.
Cinnamylideneaminoazobenzene........	orange-yellow.	purple-red.
Diphenylmethyleneaminoazobenzene.	orange-yellow.	orange-red.
Fluorenylideneaminoazobenzene	orange.	cinnabar-red.
p-Dimethylaminobenzylideneamino-azobenzene	orange-yellow.	orange-yellow.
Di-*p*-dimethylaminophenylmethylene-aminoazobenzene	orange.	orange.

It appears, therefore, that the halochromy is noticeably increased when the C:N-group is conjugated with a neighbouring C:C-group, a phenomenon which is also observed with unsaturated anils and ketones. Similarly, the hydrochloride is rendered more stable by the presence of the conjugated C:C-group. The non-appearance of halochromy in the two instances last mentioned is probably attributable to the smaller basicity of the aminoazobenzene residue as compared with the anil residue; as a consequence, salt formation may occur at a dimethylamino-group and therefore not cause halochromy. H. W.

A New Method for Preparing Esters of Amino-acids. Composition of Caseinogen. FREDERICK WILLIAM FOREMAN (*Biochem. J.*, 1919, **13**, 378—397).—The outlines of the process are as follows: The amino-acids are converted into their dry lead salts, which are suspended in absolute alcohol and converted into the ethyl esters by saturation with dry hydrogen chloride. After removal of the free hydrochloric acid and the alcohol, the ester hydrochlorides are dissolved in dry chloroform, and the free esters liberated by shaking the solution with anhydrous barium hydroxide. The chloroform is removed by evaporation under reduced pressure, and the esters are dissolved in anhydrous ether. Subsequently they are fractionally distilled in the usual manner. This process avoids considerable loss of esters by hydrolysis, which occurs by the use of aqueous solutions in the usual procedure. This method has already yielded results of value, in that some of the deficit in the amino-acid content of caseinogen has been accounted for. The author gives the following details of the percentage composition of caseinogen, partly from the results of his own work and partly from other sources: Glycine, 0·45; alanine, 1·85; valine, 7·93; leucine, 9·7; proline, 7·63; phenylalanine, 3·88; glutamic acid, 21·77; aspartic acid, 1·77; new syrups, 14·34; lysine, 7·62; histidine, 2·5; arginine, 3·81; tryptophan, 1·5; serine, 0·5; tyrosine, 4·5; hydroxyproline, 0·23; diaminotrihydroxydodecanic acid, 0·75; ammonia, 1·61; sulphur, 0·76; phosphorus, 0·85; substances of peptide nature obtained on hydrolysis, 3·41; total, 97·36%. J. C. D.

Dissociation of Oxyhæmocyanins. CH. DHÉRÉ and A. SCHNEIDER (*Compt. rend. soc. biol.*, 1919, **82**, 1038—1040: from *Chem. Zentr.*, 1920, i, 176—177).—Careful experiments with solutions of pure crystalline oxyhæmocyanin, in some cases in the presence of an antiseptic, show that the substances obtained from the snail and the lobster are readily reducible by physical dissociation. H. W.

A Compound of the Hæmocyanin of the Snail with Nitric Oxide. CH. DHÉRÉ and A. SCHNEIDER (*Compt. rend. soc. biol.*, 1919, **82**, 1041—1043; from *Chem. Zentr.*, 1920, i, 177).—A solution of the hæmocyanin forms with nitric oxide a crystalline, green dye, which is designated "hæmocyanin nitric oxide." H. W.

Liquefaction of Gelatin by Salts. T. R. BRIGGS and EVELYN M. C. HIEBER (*J. Physical Chem.*, 1920, **24**, 74—75).—Solutions of 5% gelatin were mixed with 33% solutions of zinc chloride, potassium chloride, ammonium nitrate, potassium thiocyanate and magnesium chloride, and with saturated solutions of potassium nitrate and ammonium chloride respectively, and placed in a thermostat at 19°. After thirty minutes the mixture containing potassium chloride had set to a jelly, in twenty-four hours those containing magnesium chloride and ammonium chloride had set, and after thirty-six hours the remainder were still liquid. After dialysis for twenty-four hours the whole of the solutions had set, and on again mixing with zinc chloride, ammonium nitrate, and potassium thiocyanate respectively the jellies liquefied within an hour. It is thus proved that the processes of liquefaction and gelatinisation produced by salts are strictly reversible. J. F. S.

Presence of Invertase in the Pure Honey of Bees. ALIN CAILLAS (*Compt. rend.*, 1920, **170**, 589—592).—By the general method of preparation of enzymes by precipitation with alcohol, invertase was isolated in the form of its aqueous solution from a sample of honey. The honey contained approximately 0·05% of the enzyme, which gave all the tests for invertase, including the hydrolysis of sucrose. W. G.

A Method of Testing the Amylolytic Action of the Diastase of Aspergillus Oryzæ. SELMAN A. WAKSMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 293—299).—The Lintner method for measuring the saccharogenic action of different enzymes on starch should not be used for comparative studies with different enzymes, since the end-products are not the same in the various cases. The starch liquefying (iodine) methods, with the exception of that of Wohlgemuth, do not give the "liquefaction" of starch by enzymes, but measure the reduction of the starch to substances giving no longer any reaction with iodine, which is arbitrary. In the study of the action of enzymes on the starches present or embodied in textiles (process of de-sizing), the Lintner method and its various modifications are unsuitable, since the problem consists in the elimination of starch, and not in the production of sugar. A convenient method for measuring the starch-liquefying power (amyloclastic action) of enzymes consists in adding the requisite amount of the latter to 10 c.c. of a 2% paste of raw potato starch, which is maintained at 40°, and observation of the time required for the liquid to become clear; the determination of the end-point may be facilitated by staining the starch, preferably with neutral red. When the stage of hydrolysis corresponding with this end-point is tested with iodine, it is found to be identical with that at which no heavy blue colour is obtained, but only a deep brown to faintly violet-brown colour or faint bluish-violet colour, showing that all the starch paste has been transformed into dextrins.

Comparing the starch-liquefying powers of malt enzymes and

enzymes obtained from *Aspergillus oryzae* (water extract used known commercially as polyzime), the first are found to give a higher Lintner value, whilst the second give a higher liquefying value. The ratio of the latter to the former in the case of malt preparations is 1 : 4 to 1 : 5, whilst in the case of *Aspergillus oryzae* enzyme it is 1 : 1 to 1·5 : 1, so that the liquefying power of the latter in comparison to its saccharogenic power is four to six times as great as that of the malt preparations. H. W.

Consecutive Action of Two Types of Emulsins on Amygdalin. J. GIAJA (*Compt. rend. soc. biol.*, 1919, **82**, 1196—1198; from *Chem. Zentr.*, 1920, i, 299. Compare A., 1914, i, 1099).—If the action of emulsin of almonds on amygdalin is stopped by heating at a period when a portion of the latter remains unattacked, the action can be completed by the subsequent addition of the digestive juice of *Helix pomatia*; the same amounts of hydrocyanic acid and dextrose are formed as when complete decomposition is effected by one ferment only. If the order of addition is reversed, that is, if the emulsin of almonds is added to the amygdalin solution which has been partly decomposed by *Helix* juice and then heated, complete decomposition does not occur, although a certain amount of hydrocyanic acid and of dextrose is formed. Intermediate products are formed under the influence of *Helix* juice which are not further attacked by emulsin of almonds. H. W.

Bivalent Tin as Chromophore in Aromatic Stannous Compounds and the Preparation of Hexa-aryldistannanes. ERICH KRAUSE and REINHARD BECKER (*Ber.*, 1920, **53**, [*B*], 173—190).—Alkyl compounds of bivalent tin have been described previously, but their isolation in the pure state has proved impossible. The authors have therefore turned their attention to the corresponding di-aryl compounds, which are found to be stable, crystalline substances. Their most remarkable properties are their intense colour, which must be attributed to the unsaturated tin atom behaving as a chromophore, and their peculiar transformation into hexa-aryl distannanes analogous to the hexa-alkyl compounds described by Grüttner (A., 1918, i, 159).

Tin diphenyl is prepared by the addition of finely-powdered stannous chloride to an ethereal solution of a considerable excess of magnesium phenyl bromide; it forms a bright yellow, voluminous, amorphous powder, which has m. p. 130° (to a dark red, viscous liquid), after softening at 126°. Dilute solutions of the substance in benzene are intense yellow to reddish-yellow, and become cloudy and gradually decolorised on exposure to air. The benzene solution becomes dark red, and gives a yellow precipitate on exposure to sunlight. Dry tin diphenyl is rapidly decolorised on exposure to light and air, but it may be preserved unchanged for months in an atmosphere of nitrogen. The freshly prepared material appears to have a normal molecular weight in benzene

olution, but polymerisation soon begins, so that, after a few days, he molecular weight has increased fivefold. In chloroform soluion tin diphenyl rapidly absorbs the calculated quantity of bromine nd yields tin diphenyl dibromide, which, for purposes of identifiation, was converted by potassium fluoride into the more readily urified *tin diphenyl difluoride*, colourless, four-sided rods, m. p. bove 360°.

Hexaphenyldistannane is prepared by the treatment of stannous hloride with a large excess of magnesium phenyl bromide at 100°, y the action of sodium on tin triphenyl chloride, or by reduction f the latter with sodium and alcohol; it crystallises in colourless, ectangular plates, m. p. 237° (corr.) (from benzene in colourless, hining rhombohedra + $1\cdot5C_6H_6$), and is completely stable towards ir. It has a normal molecular weight in benzene solution. It mmediately reduces silver solutions to metallic silver, even at -75°. It is converted by bromine in chloroform solution at -30° nto tin triphenyl bromide.

Tin di-p-*tolyl* is an orange-yellow, amorphous powder, m. p. 11·5°, after softening at 109°. It is less readily oxidised by air han is tin diphenyl, which, however, it closely resembles in underoing polymerisation when preserved. Possibly by reason of steric indrance, tin di-*p*-tolyl, unlike the phenyl derivatives, is not conerted into hexa-*p*-tolyldistannane when heated with an excess of agnesium phenyl bromide at 100°; at a higher temperature a omplicated decomposition occurs, tin tetra-*p*-tolyl being formed ogether with many other substances.

Tin tetra-*p*-tolyl (compare Pfeiffer, A., 1910, i, 724) is converted nto the monobromide in pyridine solution, and this is transformed nto the hydroxide; the latter is purified and transformed by the equisite halogen acid into *tin tri*-p-*tolyl chloride*, coarse, rhombic lates, m. p. 97·5°, *tin tri*-p-*tolyl bromide*, colourless rhombohedra, n. p. 98·5°, and *tin tri*-p-*tolyl iodide*, colourless, rhombic plates, n. p. 120·5°. *Tin tri*-p-*tolyl fluoride*, slender, interwoven needles, n. p. 305°, and *tin triphenyl fluoride*, colourless, minute prisms, n. p. 357°, after darkening at 345°, are also described. The latter ubstance is of interest, since it is so sparingly soluble in cold lcohol, ether, or water that the chloride can be used for the quantative precipitation of fluorides. *Hexa*-p-*tolyldistannane*, colouress, rhombic platelets, m. p. 145° (corr.), is prepared by the reducon of tin tri-*p*-tolyl bromide with sodium and alcohol.

Tin tetra-m-*tolyl* forms colourless needles, m. p. 128·5°.

The following *o*-tolyl derivatives were prepared from the product btained by the action of stannic chloride on the quantity of magesium *o*-tolyl bromide calculated for the formation of tin tetra-tolyl (instead of a considerable excess, as recommended by Krause nd Schmitz, this vol., i, 198); the crude material was purified by onversion into the hydroxide, which was subsequently converted nto *tin tri*-o-*tolyl chloride*, colourless, pointed prisms, m. p. 99·5°. *n tri*-o-*tolyl bromide*, compact, rhombic plates, m. p. 99·5°, and *n tri*-o-*tolyl iodide*, hard, rhombic crystals, m. p. 119·5°.

Tin di-p-*xylyl*, m. p. 157°, after softening at 155°, closely resembles the corresponding di-*p*-tolyl compound, but is considerably more stable towards air, so that it may be preserved exposed to air for some considerable time without undergoing change. The following *p*-xylyl derivatives are obtained in the usual manner: *tin tetra*-p-*xylyl*, colourless, microscopic, four-sided rods or cubes, m. p. 278° (corr.); *tin tri*-p-*xylyl chloride*, colourless, compact crystals, m. p. 141·5° (corr.); *tin tri*-p-*xylyl bromide*, large, six-sided crystals, m. p. 151° (corr.); *tin tri*-p-*xylyl iodide*, large, six sided plates, m. p. 159·5° (corr.); *tin tri*-p-*xylyl fluoride*, slender microscopic needles, m. p. 247° (corr.); *hexa*-p-*xylyldistannane* (from tin tri-*p*-xylyl bromide and sodium), colourless, rhombic plates, m. p. 196° (corr.).

Tin tetra-m-*xylyl* forms long, rhombic needles, m. p. 224° (corr.) it is isolated with greater difficulty than are its isomerides owing to its greater solubility. The tin tri-*m*-xylyl haloids do not crystallise with the exception of the *fluoride*, slender, interwoven needles m. p. 209° (corr.).

Tin di-a-naphthyl resembles the corresponding xylyl compound in preparation and properties, but is even less sensitive to air; it has m. p. 200° after softening at 196°. H. W.

Physiological Chemistry.

The Action of Certain Precipitates on the Solution of Red Globules. ARTHUR VERNES and ROGER DOURIS (*Compt. rend* 1920, **170**, 528—529).—The property, which the serum of pig blood possesses, of dissolving the red globules from sheep's blood can be destroyed by dissolving in the serum a precipitate formed from ferric thiocyanate and human serum. W. G.

The Physiological Action of Calcium. R. HÖBER (*Pflüger's Archiv*, 1917, **166**, 531—608; from *Physiol. Abstr.*, 1917, **2**, 523 —The effect of Ca (ions) in diminishing hæmolysis by narcotics shared by the ions Sr, Ba, and Mg. Mn and Co are more efficacious than the above, and Ni more efficacious than any of the others When, however, hæmolysis is produced by hypotonic solutions of sodium chloride, Ca is the most and Ni the least efficacious. When hæmolysis is produced by saponin, the relative inhibitory effect of the ions in question differs with the blood of different animals. In preventing (or diminishing) the toxic action of potassium on skeletal muscle, the ions work in the following order: Ca>Sr

$Mg > Co > Ba > Mn > Ni > Zn$, that is, their value corresponds with that in diminishing hæmolysis by hypotonic solutions. In preventing (or diminishing) the toxic action of narcotics on muscle, the ion series reads: $Ni > Co$, Mn, $Ba > Sr$, Ca. Further, in preventing (or diminishing) the fibrillar contractions evoked by solutions of sodium chloride, the series becomes: Ni, $Co > Mn > Ca$, $Mg > Sr > Ba$. The effect of potassium on the demarcation current of muscle is inhibited not merely by Ca, but also by Sr, Ba, Co, Mn, and Ni ions, but not by Mg. Complex cobalt and chromium ions act like Ca when they are bi- or ter-valent, but not when they are univalent. Cu, UO_2, and Cd cannot replace calcium at all; Zn, Ni, and Ce ions can only do so partly. J. C. D.

Theory of Odour. HANS HELLER (*Biol. Zent.*, 1919, **39**, 364—370; from *Chem. Zentr.*, 1920, i, 139).—Chemical and physiological considerations lead the author to consider Teudt's theory (A., *1913*, i, 607) untenable. *H. W.*

Polonium Radiation and Recovery of Function. H. ZWAARDEMAKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 383—385).—The effect of α- or β-rays in restoring cardiac action (A., 1917, i, 241) appears to be due to the direct action of the rays, rather than to their influence in determining the liberation of potassium ions from the cardiac muscle. Thus the beating of a frog's heart, which had ceased owing to removal of potassium ions from the circulating liquid, was restored when the organ was exposed to β-rays from polonium, but ceased again when potassium ions were supplied in addition, owing to the opposing effects of α- and β-rays (A., 1918, i, 326). It revived, however, when either the polonium or the potassium ions were removed. J. K.

Permeability of the Glomerular Membrane to Stereoisomeric Sugars. H. J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 351—359).—Previous investigations (A., 1919, i, 187) gave results which led the author to suspect that the retention of dextrose by the glomerular membrane was in some manner connected with the configuration of the sugar molecule.

The hypothesis that the group $\begin{matrix}\text{C·OH}\\ | \\ \text{H·C·OH}\end{matrix}$ causes retention cannot be true, for *l*-arabinose and *l*-mannose pass through the kidney, whilst *d*-galactose, *l*-xylose, and *d*-ribose are partly retained. Of all the sugars examined (hexoses and pentoses) only dextrose is completely retained by the glomerular membrane. J. C. D.

The Partial Permeability of the Glomerular Membrane to *d*-Galactose and some other Multi-rotatory Sugars. H. J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 360—373).—The multi-rotatory sugars can be divided into three groups according to their behaviour in the kidney. The first group consists of those sugars of which both modifications are retained by the glomerular membrane. Of this class only one

representative, dextrose, is known. The second group (*d*-galactose, *d*- and *l*-xylose, and *d*-ribose) are partly diffusible through the renal glomerulus, and apparently only one modification is retained. The *third* class consists of sugars, both modifications of which pass the glomerulus, such are *l*-glucose, *d*-mannose, *d*- and *l*-arabinose. In the case of the members of the second group, the retention or non-retention is governed wholly by the positions which the H and OH linked to the asymmetric C-atom occupy relatively to each other. J. C. D.

The Active Principles of the Pituitary Gland. HAROLD WARD DUDLEY (*J. Pharm. Expt. Ther.*, 1919, **14**, 295—312).—The dried and powdered gland is extracted with acidified water, and the extract purified by precipitation with colloidal ferric hydroxide. From the filtrate, by continuous extraction with butyl alcohol under reduced pressure, crystalline fractions may be obtained which possess strong physiological activity. The extract contains all the uterine stimulant, together with some of the pressor substance and contaminating substances. The view expressed by Abel and Kubota (A., 1919, i, 506) that histamine is identical with the uterine stimulant of the pituitary gland, is not confirmed. Considerable differences in the properties of these substances were observed. J. C. D.

Influence of Temperature on Narcosis of Muscle and Nerve. R. HÖBER (*Pflüger's Archiv*, 1919, **174**, 218—232; from *Physiol. Abstr.*, 1919, **4**, 184).—The depression of irritability of muscle and of conductivity in nerve by the action of various narcotics is increased by warmth and diminished by cold. The effects of potassium chloride, cocaine, and novocaine on muscular irritability are independent of temperature. The dependence of the partition coefficients of indifferent narcotics on temperature has no apparent relationship to their narcotic powers J. C. D.

Carcinolytic Organic Acids. ERNST FREUND and G. KAMINER (*Wien. klin. Woch.*, 1919, **32**, 1105; from *Chem. Zentr.*, 1920, i, 135—136).—Normal serum and normal tissue contain a fatty acid compound which is able to destroy cancerous cells, and is to be regarded as the protective substance of normal cells; it is termed the "normal acid" by the authors. Cancerous serum and tissue show a lack of normal acid, and contain in its place an unsaturated fatty acid compound which behaves as a protective material to the cancerous cell; to this the name *carcinomic acid* is assigned. At least ten times as much normal as carcinomic acid is necessary for neutralisation. Since the preparation of considerable amounts of normal acid is a matter of difficulty (5 litres of serum yield 0·1 gram of acid), the authors have attempted to replace it by acids that can be synthesised. Under similar conditions, oxalic and malonic acids are inactive, succinic acid is active, glutaric, adipic, and pimelic acids are inactive, suberic acid is again active, whilst azelaic and sebacic acids have no action. These results and those

of other experiments lead to the conclusion that the methylene group has a distinct influence on carciuolytic activity. Actually, decane-$\alpha\kappa$-dicarboxylic acid has the power of destroying cancerous cells. The minimal concentrations for succinic, suberic, and decane-$\alpha\kappa$-dicarboxylic acids are about 0·05%, 0·01%, and 0·005% respectively; a parallelism thus appears to exist between increase in activity and number of C_2H_4-groups. In connexion with *carcinomic* acid, the protective action of sterically different fatty acids towards cancerous cells has been examined. Among isomeric acids, only those substances have a protective effect in which two carboxyl groups must be assumed to be in close proximity to one another and to a carbon atom. H. W.

Significance of Potassium in the Organism. H. ZWAARDEMAKER (*Pflüger's Archiv*, 1918, **173**, 28—77; from *Physiol. Abstr.*, **4**, 80).—A summary and extension of previous work (see A., 1917, i, 241; 1918. i, 326, ii, 182) on the replacement of potassium by equiradio-quantities of other elements. Irradiation from without can replace the addition of other radio-active elements to nutritive fluids, and it is immaterial which rays are used for this, except that they cannot be used together effectively, as they are then biologically antagonistic. The equilibrium necessary for proper activity is altered by eosin and by calcium, and in the opposite direction, by fluorescein, and in summer it is immaterial whether the radio-active element which replaces potassium be present in ionic form or as a colloid complex. A frog's heart under the influence of uranium is incapable of giving extra systoles in response to electrical excitation. J. C. D.

Genesis of Thiocyanic Acid in Animals. VIII. SERAFINO DEZANI (*Arch. farm. sper. sci. aff.*, 1919, **27**, 148—160. Compare A., 1919, i, 506).—With man and the dog, just as with the rabbit, ingestion of cauliflower is followed by more or less intense elimination of thiocyanic acid in the urine. The thiocyanogenetic substance of the cauliflower is found also in the white and green forms of *Brassica oleracea L. var. capitata*. This substance appears to belong to the group of so-called extractive substances, as it is neither a protein nor an amino-acid precipitable by phosphotungstic acid, nor a thiocarbimide, nor an organic sulphide. The extractive substances of flesh contain no thiocyanogenetic substances. T. H. P.

The Important Rôle of Preluciferin. RAPHAEL DUBOIS (*Rép. pharm.*, 1919, [3], **30**, 289—291. Compare A., 1897, ii, 112; Harvey, A., 1917, i, 365; 1919, i, 299; this vol.; i, 202, 203).—The author objects to the terms photogenin and photophelein for luciferase and luciferin. Luciferase is the enzyme and luciferin the substrate concerned in biochemical oxidations with the production of light; both are thermolabile. The luciferin is used up in the reaction which produces light; but a further supply may

be made by the action of another enzyme, coluciferase, on preluciferin, which is thermostable and quite probably is an albumose. If a solution containing both luciferase and coluciferase be kept at 65°, the luciferase is destroyed. The coagulum is removed from the solution by filtration; the filtrate is mixed with a boiled solution which contains preluciferin; no light is produced. On addition of a small crystal of potassium permanganate to this solution to take the place of the destroyed luciferase, light appears at once, since the coluciferase has made luciferin from the preluciferin. Photophelein may be used as a generic name for mechanical, physical, and chemical agents which favour, activate, or excite the reaction between luciferase and luciferin. Such agents are agitation in the presence of oxygen, dilution with aerated water, heat, compounds with an alkaline reaction (ammonia, sodium carbonate, alkaloids, amines), ethyl ether, etc.; these agents have no action on solutions in which potassium permanganate does not disclose a trace of luciferin.

CHEMICAL ABSTRACTS.

Bioluminescence. XII. The Action of Acid and of Light in the Reduction of Cypridina Oxyluciferin. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1920, **2**, 207—213. Compare this vol., i, 202, 203).—The addition of acid to a boiled extract of cypridina (oxyluciferin) causes the formation of a substance (luciferin), which will give light with luciferase. It would seem, however, that the action of bacteria, yeast, muscle cells, etc., on oxyluciferin must be due not entirely to their acid reaction, but to their reducing power as well. The processes which occur in this reaction are compared with the reduction of methylene-blue, and a scheme co-ordinating the various factors which influence this example of bioluminescence is advanced.

J. C. D.

Behaviour of Benzoylpropionic Acid, Phenylethyl Alcohol, and Phenoxyacetic Acid in the Organism of Man and Dog. H. THIERFELDER and E. SCHEMPP (*Pflüger's Archiv*, 1917, **167**, 280—288; from *Physiol. Abstr.*, 1917, **2**, 465).—The first-named keto-acid is reduced to a hydroxy-acid, and of this the *l*-form is largely excreted as such; a portion of it is further changed. The *d*-form is reduced to phenylbutyric acid, and thus is partly, by *β*-oxidation, converted into phenylacetic acid, which unites with glutamine. A small amount of the keto- or hydroxy-acid is probably excreted in union with glycine. Phenylethyl alcohol is oxidised to phenylacetic acid. Phenylacetaldehyde given subcutaneously is excreted as phenaceturic acid. Phenoxyacetic acid is not a metabolic product. Most of it is recoverable as such from the urine.

J. C. D.

Pharmacological Action of Ketocineole. GUIDO CUSMANO (*Gazzetta*, 1919, **49**, ii, 228—232).—Similar chemical behaviour is shown by camphor and ketocineole, which differ in molecular structure as regards the nature of the bridge uniting the tertiary

and quaternary carbon atoms. In their physiological effects, however, these two compounds exhibit differences. The psychomotor excitation produced in man and other mammifers by camphor appears only in embryo on administration of ketocineole, and is mostly masked by symptoms in which depression of cerebral activity is prominent. The differences are more distinct in the case of the frog; here the initial curaric action of camphor which prevents the development of the convulsions observed in warm-blooded animals, is not produced by ketocineole. T. H. P.

Influence of Temperature and Concentration on the Toxicity of Solutions, particularly of Electrolytes. O. HARTMANN (*Pflüger's Archiv*, 1918, **170**, 585—645; from *Physiol. Abstr.*, 1918, **3**, 573).—In an extensive series of experiments on *Bosmina longirostiris*, O.F.M., a member of the Cladocera, the effect on the duration of life at ten different concentrations of various acids, inorganic salts, organic salts, and alcohols was studied at temperatures of 0°, 13°, 18°, and 30°. Toxicity curves for the various concentrations and temperatures are figured. The toxicity concentration curve resembles more or less closely the adsorption isotherm of the various substances. The specific toxicity of the substances concerned is responsible for the form and the specific course of the curve. The osmotic pressure, however, tends to shorten life in the higher concentrations of the mildly toxic substances, and determines the acute bend above a certain critical concentration in the case of these curves. The diminishing toxicity of the anion and univalent cation series shows a close correspondence with the known series. The toxicity of the individual substances diminishes on dilution in varying degrees; those with similar or identical toxicity concentration quotients show little change in their relative position, whereas those with widely different quotients exhibit the greatest change in their relative toxicity on dilution. A similar formula for the temperature–toxicity curve is given, but its untrustworthiness is indicated by the variety of constants yielded at different temperatures. The relation of the absolute value of temperature-coefficient (Q_{10}) and its peculiar progress were subjected to a very searching analysis. The very high values often observed at the maximum and minimum temperatures are due to complicated physiological changes in the living system, which are rapidly completed on changes at the temperatures in question. Owing to the very different temperature-coefficients and temperature-toxicity coefficients of the various substances, changes in toxicity occur at different temperatures; substances with similar temperature-toxicity quotients maintain their relative position in the series, whereas those with different quotients alter their relation on changes of temperature. The form of the toxicity–concentration curve is sometimes different for different temperatures, as higher temperatures usually determine a more gradual rise in the duration of life on dilution. Hence the adsorption formula constants will apparently be different at different temperatures. The value of the tempera-

ture-coefficient is also apparently influenced by the concentration of the experimental fluid. A general formula, including concentration, temperature, and duration of life, was constructed from the individual formulæ; its accuracy, however, is only approximate, and varies greatly for the various substances. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Butylene Glycol Fermentation of Sugar by Bacillus anthracis. M. Lemoigne (*Compt. rend. soc. biol.*, 1919, **82**, 984—986; from *Chem. Zentr.*, 1919, iii, 1018. Compare this vol., i, 122).—Fermentation of sugar by three different varieties of *B. anthracis* gave distillates containing a small amount of a reducing agent which yielded diacetylosazone with phenylhydrazine, and is therefore regarded as acetylmethylcarbinol; $\beta\gamma$-butylene glycol could not be detected. The phenomena are thus analogous to those observed with the *B. subtilis* group; whilst, however, in the latter case the $\beta\gamma$-butylene glycol collects in the cultures, it is immediately transformed by *B. anthracis* into lactic acid, and cannot be detected even as a transitory phase. The author is led to the conclusion that lactic acid and butylene glycol are intermediate products of the same process of fermentation which follows a different course with *B. anthracis* and *B. subtilis*. H. W.

Cycloclastic Power of Bacteria. I. A Quantitative Aerobic Decomposition of Histidine by Bacteria. Harold Raistrick (*Biochem. J.*, 1919, **13**, 446—458).—The bacterial decomposition of histidine was followed by studying the fate of the nitrogen groups. *B. paratyphosus A*, *B. paratyphosus B*, *B. faecalis alcaligenes*, and *B. pyocyaneus* can produce ammonia from both the amino-group of the side-chain and from the iminazole nucleus of the histidine molecule. With *B. proteus vulgaris* ammonia is formed only from the side-chain nitrogen, and it appears probable that this organism cannot break down the ring structure.

J. C. D.

Respiratory Process of Nitrifying Bacteria. III. The Respiration of the Nitrite Organisms and the Influence of Chemical Substances. O. Meyerhof (*Pflüger's Archiv*, 1917, **166**, 240—280; from *Physiol. Abstr.*, 1917, **2**, 207).—The material used was obtained from a pure culture of *Nitrosomonas*, and Winogradsky's solution was employed as a culture medium.

maUnder favourable conditions cultures were obtained which in and ty-four hours could oxidise ·4 grams of ammonium sulphate azelaicre to nitrite. The rate of respiration depends on the concen-

tration of the ammonium salt, the optimum being at a concentration of $N/200\text{-}NH_4$, whilst it is zero in a concentration of $N/10\text{-}NH_4$. The accumulation of the nitrite ion retards respiration, and growth stops when the concentration of this ion reaches $0{\cdot}25N$. With decreasing partial pressure of oxygen there is decreasing respiration from about one-third atmospheric pressure downwards. The H-ion concentration strongly influences the respiration rate; the optimum is in a concentration of $P_H = 8{\cdot}4$ to $8{\cdot}8$; outside the limits $P_H = 9{\cdot}4$ and $P_H = 7{\cdot}6$ no respiration takes place.

The rate of respiration is very sensitive to alkali and alkaline-earth salts, and the heavy metals are very toxic. Respiration and growth respond differently towards nitrogen-free organic substances. Dextrose retards growth in $0{\cdot}001M$-solution, but respiration is not retarded in $0{\cdot}2M$. Methyl alcohol is more toxic than ethyl alcohol. J. C. D.

The Free Energy of Biological Processes. GEORGE A. LINHART (*J. Gen. Physiol.*, 1920, **2**, 247—251).—From considerations of energy exchange it is concluded that only about 1% of the total available energy is utilised in the fixation of nitrogen by *Azotobacter*, growing in a 0·1 molar solution of mannitol.

J. C. D.

Nitrogen Metabolism in Saccharomyces cerevisiæ. LESLIE HERBERT LAMPITT (*Biochem. J.*, 1919, **13**, 459—486).—Excess of yeast ensures the removal of the greatest total amount of nitrogen. During active fermentation, the greater the coefficient of multiplication, the greater the amount of nitrogen assimilated by each cell. Active reproduction may result in a lowering of the nitrogen coefficient, but the final coefficient is independent of the initial value, tending to reach a constant value for any particular conditions of reproduction. The action of yeast on asparagine may result in the production of malic acid, the ammonium salt of which is readily fermented, with the production of ethyl alcohol. Propionic acid and its ammonium salt are not fermented (compare Effront, A., 1908, i, 491; 1909, ii, 255). Fermentative activity is essential to nitrogen assimilation, but, once induced, the deamination may continue after zymatic activity ceases. During fermentation, yeast loses nitrogen to the medium. This process, which has been termed "nitrogen excretion," is dependent on the life of the cell, and takes place even when nitrogen is being assimilated. The substances which are excreted can be used as a source of nitrogen by the yeast under suitable conditions. Increase in the amount of sugar available increases the rate of excretion, but there is no proportion between zymatic activity and such excretion.

J. C. D.

Influence of Substances Extracted from Yeast on the Fermentation of Carbohydrates by Yeast. EMIL ABDERHALDEN (*Fermentforsch.*, 1919, **3**, 44—70; from *Chem. Zentr.*, 1920, i, 16. Compare Abderhalden and Schaumann, A., 1919, i, 108).—The influence of yeast extract is proved in a series of

experiments in which equal amounts of yeast are allowed to act on equal weights of carbohydrate, and fresh amounts of the latter are added as soon as the evolution of carbon dioxide markedly slackens until further addition does not cause renewed fermentation; in these circumstances, much more sugar is fermented in the presence of alcoholic yeast extract than is otherwise the case. Simultaneously, the rate of fermentation is greatly increased, generally to a considerably greater extent than by fructosediphosphoric acid. The yeast cells also increase more rapidly, but the greater activity which is thus indicated is not sufficient to account entirely for the action of the yeast extract, since the activating effect is also observed when expressed juice or dry yeast is used. H. W.

Observations on Yeast (mainly Munich Brewery Press Yeast). T. BOKORNY (*Pflüger's Archiv*, 1916, **164**, 203—273; from *Physiol. Abstr.*, 1916, 1, 453).—In keeping with the fact that sucrose is more readily fermented than dextrose, the previous treatment of yeast with antiseptics destroyed its capacity to ferment the latter, but not the former sugar or maltose. Glycerol may be included among the adequate sources of carbon for the growth of yeast. When added to a nutrient medium containing sugar, ammonium sulphate, and salts, an increase of 30 to 42% in the dried weight was observed at the end of three days, as compared with 9% in the control culture. The substitution of peptone or amino-acids for the ammonium salt gave similar results. Although the capacity of furnishing the aldehyde atom-complex is probably the determining factor in the utilisation of carbon, formaldehyde and other aldehydes were not assimilated by the yeast cell.

Peptone is an excellent source of nitrogen, and its addition to a medium containing sugar and salts resulted in an increase of 163% in the dried weight after the lapse of three days; glycine was the least satisfactory of the amino-acids examined, and yielded an increase of only 19%.

Although large quantities of fat have been found in involuting yeast, no appreciable increase in the fat content occurred even when yeast was cultivated in the most favourable medium (peptone and sugar solution).

The study of certain injurious factors showed that yeast was not destroyed by freezing or by drying at the ordinary temperature for eight days; prolonged drying killed the yeast, but did not destroy the zymase. Neutral salts in saturated solution usually prevented fermentation within a few days. The injurious effects of a number of organic and inorganic acids, both on the cell and on zymase activity, are recorded. J. C. D.

The Chemistry of Alcoholic Fermentation. ERNST ZERNER (*Ber.*, 1920, **53**, [*B*], 325—334).—The author gives an account of the manufacture of glycerol by the Connstein-Lüdecke process (A.,

1919, i, 463) during the war in Austria-Hungary, which is also of interest, since some of the conclusions are at variance with those arrived at by Neuberg and Reinfurth (this vol., i, 125). The most important results are as follows. Equivalent amounts of glycerol and acetaldehyde are produced in the process; in addition, alcohol and carbon dioxide are formed, and these are the only substances obtained in appreciable amount. Increase in the amount of sodium sulphite increases the yield of glycerol and acetaldehyde, but more than 38% of glycerol cannot be obtained. Sodium sulphite may be replaced by sodium hyposulphite. Failure to produce glycerol in quantitative amount by sufficiently increasing the relative proportion of sulphite has been attributed by Neuberg to dissociation of the aldehyde–bisulphite compound; this conclusion appears to be unfounded, since with moderate additions of sulphite the equivalent amount of glycerol is almost obtained, whilst with very large additions (which should have the effect of suppressing dissociation of the aldehyde–bisulphite compound) the yield of glycerol sinks to about two-thirds of that theoretically possible. The effect seems rather to be attributable to the fact that action between aldehyde and bisulphite is not an instantaneous process, and that a certain amount of opportunity is thus offered for further degradation of the aldehyde and glycerol to alcohol and carbon dioxide.

At first sight, it seems reasonable to suppose that pyruvic acid is an intermediate stage in the fermentative conversion of sugar into aldehyde and glycerol, and Neuberg has shown that the acid can actually be fermented in the presence of sulphite. In these experiments, he has only used one-eighth to one-fourth the equivalent amount of the sulphite; the use of larger proportions, however, shows that the bisulphite compound of pyruvic acid is not fermentable, and that neither pyruvic nor glyceric acid can constitute the intermediate stage in the production of aldehyde by alcoholic fermentation.

When sugar is fermented in the presence of sodium thiosulphate, sulphur is soon precipitated, hydrogen sulphide is evolved, and, after a time, fermentation ceases; the yield of glycerol, reckoned on the sugar actually fermented, is very considerable. When the experiments are repeated with the addition of sodium sulphite or sodium hydrogen carbonate, reaction proceeds as if the thiosulphate were not present. It appears, therefore, that an acid is produced during fermentation which decomposes the thiosulphate according to the equation $Na_2S_2O_3 + HX = NaHSO_3 + NaX + S$. The sulphur is converted into hydrogen sulphide by the reducing action of the yeast, whilst the sodium hydrogen sulphite combines with the aldehyde, and thus provides the possibility of a good yield of glycerol. Fermentation is stopped owing to the production of organic sulphur derivatives, which poison the yeast. In the presence of sulphite or carbonate, the acid is neutralised by these, and the thiosulphate remains undecomposed. Generally, it may be stated that glycerol and aldehyde are intermediate products of

alcoholic fermentation which are simultaneously formed, and, in normal circumstances, simultaneously disappear; as a preliminary phase, an acid must be formed, which, however, is not identical with pyruvic acid.

During normal fermentation (without sulphite), the maximum amount of aldehyde appears to be present in the middle period of action. H. W.

The Regulator System: Primary Phosphate-Bicarbonate-Free Carbonic Acid, in place of the System: Primary Phosphate-Secondary Phosphate. W. Windisch and W. Dietrich (*Woch. Brau.*, 1920, **37**, 81—83).—The lowering of surface tension of aqueous solutions of eucupine dihydrochloride, which results from the liberation of the free base by alkalis (compare Traube, A., 1915, ii, 571), has been used as a means of investigating the equilibrium in the reaction $K_2HPO_4+CO_2=KH_2PO_4+KHCO_3$ in dilute aqueous solutions. It is concluded that in presence of excess of carbon dioxide the reaction proceeds practically to completion from left to right. *In living and breathing tissues, therefore, and in fermenting liquids, phosphates must be present entirely as primary salts in equilibrium with potassium hydrogen carbonate and carbon dioxide. Only when respiration or fermentation has ceased and there is no longer an excess of carbon dioxide can dipotassium phosphate exist in equilibrium with the monopotassium salt.* J. H. L.

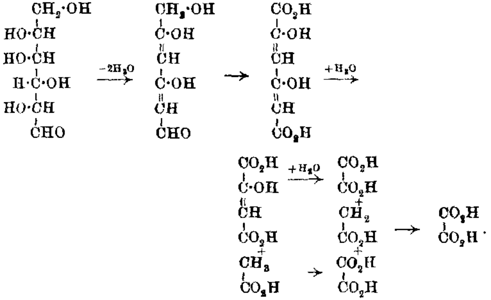
Mechanism of the Formation of Oxalic Acid by Aspergillus niger. Harold Raistrick and Anne Barbara Clark (*Biochem. J.*, 1919, **13**, 329—344).—Good yields of oxalic acid were obtained when *Aspergillus niger* was grown in the presence of the four-carbon dibasic acids, this being especially true in the case of succinic, fumaric, and malic acids. Very little oxalic acid was produced from sodium maleate, a result which is in agreement with Buchner's observation that *A. niger* can utilise fumaric acid, but not maleic acid, as a source of carbon.

When the four-carbon monobasic acids were examined, there was very little growth of the mould and no production of oxalic acid.

Unexpected results were obtained in the case of the three-carbon acids. In almost all cases there was good growth of the organism, but practically no production of oxalic acid. Of the two-carbon acids, acetic acid behaved differently from glycollic and glyoxylic acids in giving rise to a considerable production of oxalic acid.

Growth of *A. niger* was good in media containing formic acid, but no production of oxalic acid was apparent. A consideration of these results leads the authors to conclude that the breakdown of the sugar molecule by *A. niger* does not take place by a primary splitting of one molecule of sugar into two molecules of a three-carbon acid. Neither can it occur as a gradual breakdown of the molecule carbon by carbon, for this would not give rise to the large [illegible] of oxalic acid unless the micro-organism can synthesise this

acid from one-carbon compounds, and the authors present evidence that this does not occur. The decomposition probably takes place in two stages, and may be illustrated by the following scheme:



The evidence in support of these changes is discussed. J. C. D.

Colloidal Chemistry of Cell Division. JOSEF SPEK (*Koll. Chem. Beihefte*, 1920, **12**, 1—91).—A number of experiments on the effect of salts of lithium, potassium, magnesium, and calcium on the cell division of *Paramœcium caudatum*, *P. aurelia*, and *Stylonichia mytilus* are described. It is shown that salts can either delay or accelerate the cell division by changing the swelling conditions of the colloidal plasma, or they can hinder the division by accumulating in the inside of the cells. Salts which have a very strong influence on the swelling of colloids are also capable of effecting a marked change in the velocity of cell division. Salts which have two ions, each possessing a strong swelling action, accelerate the rate of cell division to a marked extent. Such salts as lithium bromide, lithium chloride, and potassium thiocyanate possess this property to a marked degree. That these salts accelerate the plasma swelling of the *Paramœcia* is seen by the increase in volume of the organisms. Salts which reduce the swelling, such as calcium chloride and the sulphates, retard the cell division to a marked extent. The sulphates increase in their retarding action in the order Li>K>Na. In the case of lithium sulphate, it is possible that the accelerating influence of the cation may outweigh the retarding influence of the anion. In the case of the chlorides, the influence of the cations follows the order Li>Na>Ca, which is the same as the order in which they produce swelling. Potassium chloride, which accelerates the swelling of *Paramœcia* more strongly than sodium chloride, has a much less effect than lithium chloride and potassium thiocyanate, and sometimes it retards the cell division. This is explained by the greater

ease with which this salt passes inside the cells, or, in other words, it is due to a too large increase in salt content of cells in media containing potassium chloride. Sodium chloride has much less power of penetrating the cell wall. The very powerful action of lithium chloride and potassium thiocyanate is due to their coagulating influence on the surface of the cell body without affecting the interior of the cell. In the case of magnesium salts, both the chloride and the sulphate have a very indifferent action, which is due to a slight penetration of the salt. No single experiment points to cell division being effected by the withdrawal of water, that is, cell division is not an osmotic phenomenon. The addition of a substance, capable of swelling, to the culture medium, for example, gelatin, retards the cell division. Different species of *Paramœcia* behave differently towards salts. The difference is attributed to varying permeability of the cells and a dissimilar swelling capacity of the plasma. The experimental results lead to the following hypothesis. The swelling of the plasma colloids, before the cell division, is brought about by the appearance of a base, which is a by-product in the synthesis of the nuclein. The increased permeability during the cell division is accompanied by an increase in the salt content of the cell which compensates the action of the base. An increase in the salt concentration above a given quantity stops the cell division. The formation of substances possessing good swelling properties in the cell occasions new cell division. The swelling of the colloids promotes the gas exchange and the hydrolytic processes in the cell. Every cell division leads more or less completely automatically to further cell divisions. J. F. S.

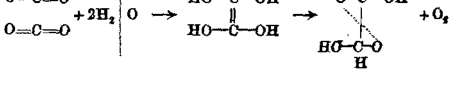
The Glycerophosphatase of Seeds. ANTOINE NĚMEC (*Bull. Soc. chim.*, 1920, [iv], **27**, 153—158).—The author has recently shown (this vol., i, 268) that glycerophosphatase is very widespread in plant cells and in the tissues of ungerminated seeds. It is now shown that this enzyme acts best in an acid medium, the optimum action being obtained with an acidity of approximately 0·06*N*. The velocity of the action which the enzyme produces indicates that it is a bimolecular action. W. G.

The Assimilation Problem. GERTRUD WOKER (*Pflüger's Archiv*, 1919, **176**, 11—38; from *Chem. Zentr.*, 1920, i, 90).—Carbon dioxide is a very inert substance, and, in its ordinary form, is only very slightly attacked by reducing agents. If reaction is to occur, it is necessary for it to suffer change in its molecular structure. "This probably occurs by isomerisation, with the formation either of a primary peroxide, $\mathrm{C}{\ll}{\mathrm{O} \atop \mathrm{O}}$, or of a secondary peroxide, $\mathrm{C}{<}{\mathrm{O} \atop \mathrm{O}}$, which, by addition of water, yields $\mathrm{C}{<}{\mathrm{O{-}OH} \atop \mathrm{OH}}$." It is found that bicarbonates and carbonates at the moment of their production or disappearance are more reactive than the ordinary

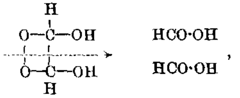
salts. A yellow coloration is produced when a mixture of potassium and sodium hydrogen carbonates and the corresponding normal carbonates in the presence of methyl alcohol is exposed to intense sunlight; the solution reduces Fehling's solution, but the presence of sugar could not be established. The corresponding carbonates and hydrogen carbonates alone do not behave in a similar manner. According to the author, assimilation is made up of a reduction phase and a subsequent combination phase. Assuming the occurrence of isomerisation and the formation of a secondary peroxide, $>C<^{O\cdot OH}_{OH}$, a compound is formed which tends to eliminate oxygen, and thereby to yield the group $>CH\cdot OH$, which is predisposed towards condensation. "Assuming the formation and immediate further utilisation of the unsaturated radicle $>CH\cdot OH$ (which is tautomeric with formaldehyde), a number of difficulties inherent to Baeyer's formaldehyde hypothesis are circumvented without losing the advantages of the latter." The formation of formaldehyde or its desmotrope from methyl alcohol and carbon dioxide can, in the presence of excess of the latter, lead to the production of dihydroxyacetone, which may be of importance for the synthesis of sugars, and, by reduction, for the formation of glycerol. Reductions with methyl alcohol are of considerable interest, since the latter is widely distributed in nature and chlorophyll is an ester of methyl alcohol. The author shows, further, how the following substances may arise by the union of $>CH\cdot OH$ groups in the "condensation-phase": dextrose, lævulose, inositol, the γ-pyrone ring, furfuraldehyde, pyrogallol, quinol, *etc.* The same group can also react with ammonia, possibly derived from formhydroxamic acid, to yield the alkaloids of the pyrrolidine or piperidine series. The rôle of chlorophyll in assimilation is discussed, the author assuming that it sensitises the isomerisation of the carbon dioxide and acts as a catalyst in the condensation phase; an intermediate union of the $>CH\cdot OH$ group with the magnesium atom of the chlorophyll appears most probable, and explains the formation of optically active substances from initially inactive material, since union occurs with an asymmetric substance, namely, the chlorophyll dye.

H. W.

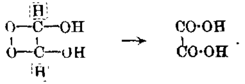
New Theory of Carbon Dioxide Assimilation. P. R. KÖGEL (*Zeitsch. wiss. Photochem.*, 1920, **19**, 215—223).—A theory of the assimilation of carbon dioxide by plants is put forward. The action of light is to polymerise the carbon dioxide, which with hydrogen then forms tetrahydroxyethylene, which passes over into the *keto-form*, thus:



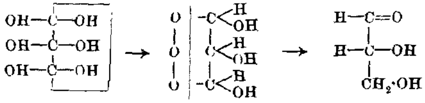
This compound contains the characteristic sugar groupin $HO-\overset{H}{C}-O$. The formation of the plant acids, formic and oxalic, i easily deduced from diketoethyl dioxide. In the case of formi acid, it is a simple splitting of the molecule,



whilst in the case of oxalic acid the removal of two hydrogen atom is necessary.

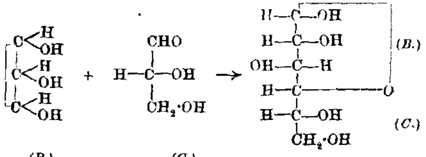


If, instead of two molecules of carbon dioxide, three undergo phot polymerisation, then glyceraldehyde is produced,



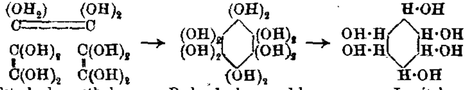
(*B.*)

and the glyceraldehyde combines with *B*, with the loss of thre oxygen atoms, to form dextrose.



(*B.*) (*C.*)

The formation of inositol on this hypothesis is represented a follows:



Tetrahydroxyethylene. Dodecahydroxycyclohexane. Inositol.

J. F. S.

The Absorption of Calcium by the Roots of Plants and its Antitoxic Properties with respect to Copper. L. Maquenne and E. Demoussy (*Compt. rend.*, 1920, **170**, 420—425. Compare A., 1917, i, 530).—Calcium, even in excess, does not prevent the absorption of copper by the roots of plants or its diffusion into their aerial organs. Similarly, copper does not prevent the assimilation of calcium. The poisonous effect of copper is not due, therefore, to its depriving the young plant of one of its essential nutrients. The antitoxic action of calcium with respect to copper is physiological, and not due to its preventing the penetration of the metal. The explanation probably lies in the fact that the calcium favours the evolution of the plant, giving it greater vigour, and in particular giving it greater volume, into which the copper diffuses, thus preventing, within certain limits, all dangerous accumulation of this latter metal. W. G.

Some Factors Affecting the Concentration of Electrolytes in the Leaf Sap of Syringa vulgaris. T. G. Mason (*Sci. Proc. Roy. Dubl. Soc.*, 1919, **15**, 651—666. Compare Dixon and Atkins, A., 1916, i, 108).—The determination of the concentration of electrolytes of the cell by means of conductivity observations is unsatisfactory unless allowance is made for the viscosity of the sap, and to this extent Chandler's results (compare *Missouri Agric. Exp. Stat. Res.*, 1914, *Bull.* No. 14) are incorrect. The application of the linear viscosity correction as a means of ascertaining the quantity of electrolytes in the sap is liable to be misleading, and recourse must be had to ascertaining the loss in conductivity which takes place in some salts, such as potassium chloride, after solution in the sap.

Considerable fluctuations in the concentrations of electrolytes in the leaf sap of *Syringa vulgaris* trees growing in different localities have been found. There appears to be a general tendency for the concentration of electrolytes to vary inversely with that of the non-electrolytes. It is suggested that these fluctuations are associated with the rate of carbon assimilation, which determines the rate at which electrolytes are removed from solution in metabolism. It is shown that the concentration of salts in the ascending sap is not responsible for these fluctuations. W. G.

Fat-soluble Vitamine. IV. The Fat-soluble Vitamine Content of Green Plant Tissues, together with some Observations on their Water-soluble Vitamine Content. H. Steenbock and E. G. Gross [with co-operation of Mariana T. Sell] (*J. Biol. Chem.*, 1920, **41**, 149—162. Compare this vol., i, 274).—Five % of clover or lucerne as the sole source of fat-soluble accessory factor in the diet of a rat will permit normal growth and reproduction. Lettuce, spinach, and chard contain the accessory factor in amounts of the same order, but, of these, lettuce appears to be the poorest. In harmony with the theory that fat-soluble *A* is associated with certain yellow plant pigments is the fact that

cabbage does not contain much of the accessory factor (*loc. cit.*). Fifteen % of lucerne, clover, and cabbage supplied sufficient water-soluble *B* for growth of young rats. J. C. D.

Fat-soluble Vitamine. V. Thermostability of the Fat-soluble Vitamine in Plant Materials. H. STEENBOCK and P. W. BOUTWELL [with co-operation of MARIANA T. SELL and E. G. GROSS] (*J. Biol. Chem.*, 1920, **41**, 163—171).—The fat-soluble vitamine in yellow maize is apparently unaffected by heating three hours under 7 kilos. pressure. Neither does this treatment cause appreciable destruction of the factor as found present in chard, carrots, sweet potatoes, or squash.

No deleterious action of the ensiling process on the fat-soluble accessory factor was detected. The experiments indicate that the accessory substance, as it occurs in grains, leaf and stem tissue fleshy roots, and curcubitous vegetables, is comparatively thermo stable. J. C. D.

The Ability of Plants to Form Optical Antipodes. KUR HESS and WILHELM WELTZIEN (*Ber.*, 1920, **53**, [*B*], 119—129).—See this vol., i, 328.

Occurrence of Chlorogenic Acid in Araliaceæ an Gorter's Reaction. A. W. VAN DER HAAR (*Pharm. Weekbla* 1920, **57**, 194—195).—Leaves of ordinary ivy (*Hedera helix*) ar of various members of the *Araliaceae* were tested for the presen of chlorogenic acid by the method given by Gorter (A., 190 i, 588). Ivy leaves alone gave a faint positive reaction; the othe gave no reaction. The *Araliaceae* examined were of Europe growth; those which Gorter found to contain chlorogenic acid we obtained from the East Indies (A., 1909, i, 935). W. S. M.

Origin and Transformation of Inulin in Articho Tubers. H. COLIN (*Bull. Assoc. Chim. Sucr.*, 1919, 3 121—126).—The leaves of the artichoke (*Helianthus tuberosus*) free from inulin at all stages of growth. They contain sugars a starch, and are as rich in starch as the leaves of the potato pla Formation of inulin takes place in the stem, throughout its wh length, and is completed in the tubers. The inulin must be p duced chiefly from dextrorotatory carbohydrates supplied by leaves. There is practically no difference between young mature tubers in respect of the nature of the carbohydrates p sent. The rotatory power of the juice of the tubers undergoes appreciable change between August and November, but afterwa approaches zero, and finally becomes positive, owing to the version of inulin into lævosans of lower molecular weight and formation of sucrose. When the new plant begins to develop, inulin passes into the stem chiefly in the form of reducing suga J. H.]

Fatty Acids of Earthnut Oil. A. HEIDUSCHKA and S. FE (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 241—265).—The fatty a

obtained from a specimen of earthnut oil had the following composition: arachidic acid 2·4%, lignoceric acid 1·9%, stearic acid 4·5%, palmitic acid 4·0%, oleic acid 79·9%, and linolic acid 7·4%. The oleic acid probably included a small quantity of hypogæic acid. W. P. S.

Cyanogenesis in Sudan Grass: a Modification of the Francis-Connell Method of Estimating Hydrocyanic Acid. PAUL MENAUL and C. T. DOWELL (*J. Agric. Res.*, 1920, **18**, 447—450).—A determination was made of the amount of hydrocyanic acid in Sudan grass in freshly-cut samples at intervals of a week during the season. The amount obtained was found to be 0·0105% in the fresh plant, only a third of that contained in the grain sorghums. The amount was determined by finely dividing the grass and leaving it with water at 40° for two hours. After this it was made strongly acid with tartaric acid, and distilled into 30 c.c. of 2% sodium hydroxide. The cyanide was precipitated as Prussian-blue, which was burned in a muffle furnace and weighed.

The colorimetric method of Francis and Connell for the estimation of hydrocyanic acid (A., 1913, i, 1284) was investigated and improved, as follows. The distillate containing the hydrocyanic acid is evaporated with 1 c.c. of concentrated yellow ammonium sulphide at 70°. The residue is heated at 130°, dissolved in 10 c.c. of warm water acidified with hydrochloric acid, and calcium chloride solution added drop by drop until the sulphide ceases to form; then 10% ferric chloride solution is added until the red colour is permanent. The solution is then filtered, and 5 c.c. of ferric chloride solution added to the filtrate. The heating at 130° is found to prevent colloidal sulphur going into solution, and the addition of the second quantity of ferric chloride produces the maximum intensity of colour. No change in this intensity is produced by the addition of electrolytes. A standard solution was prepared from a standard solution of potassium cyanide in a similar manner, and the two solutions were compared in a Bock-Benedict colorimeter. J. H. J.

Hydrocyanic Acid Content of Phaseolus lunatus. H. LÜHRIG (*Chem. Zeit.*, 1920, **44**, 166—167).—Beans of the *Phaseolus lunatus* species were found to yield small quantities of hydrocyanic acid when steeped for several hours in water, then macerated, acidified with tartaric acid, and steam distilled. The distillate was collected in dilute silver nitrate solution; and since sulphur compounds also distilled, it was found necessary to dissolve the silver cyanide in ammonia, separate the silver sulphide by filtration, and reprecipitate the silver cyanide by the addition of nitric acid. The silver cyanide was then collected, ignited, and the residue of metallic silver weighed. Nine samples of the beans examined yielded from 5·1 to 23·4 mg. of hydrocyanic acid per 100 grams of beans. The beans did not produce any poisonous effect when eaten in large quantity, provided that they had been

properly steeped in water, washed, and boiled for three hours. Treatment with emulsin during the steeping operation did not increase the amount of hydrocyanic acid yielded to any appreciable extent.
W. P. S.

Constituents of the Seeds of Pharbitis nil chois. Y. Asahina and S. X. Terada (*J. Pharm. Soc. Japan*, 1919, **452**, 821).—From the seed of *Pharbitis nil chois* (*P. hederacea chois*, *P. triloba*, Miq., *Ipomea triloba*, Th.) (the Chinese drug "Ch'ien-niu-tzu"), the authors have isolated 3·44% of the resin glucoside pharbitin, m. p. about 145—155°, darkening at 134°, $[\alpha]_D$ −43·53° (acetyl derivative, m. p. 115—120°, softening at 110°, $[\alpha]_D$ −18·87°), which yields by hydrolysis (1) a fatty acid which is volatile with steam (possibly a valeric acid with some tiglic acid), (2) the non-volatile *nilic acid* (*barium* salt,

$$C_{10}H_{18}O_6Ba,2H_2O),$$

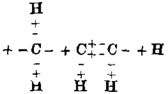
and (3) pharbitic acid, m. p. 155—162°, $[\alpha]_D$ −47·61° (Kromer, A., 1897, ii, 68, gives m. p. 156—162° and $[\alpha]_D$ −46·62°). The hydrolysis of pharbitic acid by 5% sulphuric acid yields dextrose, a pentose (osazone, m. p. 172°; possibly methylpentose), and an acid identical with ipurolic acid obtained by Power and Rogerson from *Ipomœa purpurea* (A., 1908, ii, 725).
Chemical Abstracts.

Chemical Constituents of Malt Germs, especially Hordenine. Yoshitaka Hashitani (*J. Tokyo Chem. Soc.*, 1919, **40**, 647—667).—The air-dried germs contain water 10·21, ash 3·02, crude protein 21·49, pure protein 13·32, crude fat 3·19, crude fibre 18·40, soluble non-nitrogenous substances 43·69, reducing sugar (calculated as dextrose) 3·65, non-reducing sugar 1·02, pentosan 18·42, methylpentosan 1·05, and cellulose 12·04%. The cell wall is shown by microchemical examination to contain mainly cellulose, which, after hydrolysis with 3% sulphuric acid, responded with tests for xylose, dextrose, lævulose, and galactose. The dried malt germ contains 4·65% of nitrogen. Of the total nitrogen, 6·67% corresponds with water-soluble protein nitrogen, 56·77% with pure protein nitrogen, 20·22% with amino-acid nitrogen, 23·01% with diamino-acid, purine base, and other nitrogen. The air-dried material contains 0·11 of asparagine and 0·13% of hordenine. The sulphate of the latter forms colourless needles, m. p. 209—211°; the hydrochloride has m. p. 176·5—177·5°, the hydrobromide m. p. 173—174°, the hydrogen tartrate m. p. 170—171°, the normal tartrate m. p. 180—181°, the hydriodide m. p. 227—228°, and the methiodide m. p. 179—180°. Benzoylhordenine, m. p. 47—48°, forms a hydrobromide, m. p. 171—172°, and a sulphate, m. p. 270—271°.

Alcoholic fermentation is accelerated by the addition of 0·005%, but is stopped completely by 1·28% of hordenine.
Chemical Abstracts.

Organic Chemistry.

The Electronic Constitution of Normal Carbon Chain ompounds, Saturated and Unsaturated. EUSTACE J. CUY ·OUYUMDJOPOULOS) (*J. Amer. Chem. Soc.*, 1920, **42**, 503—514). -A theory of the constitution of carbon chain compounds is put orward, based on the conceptions of Hanke and Koessler (A., 919, i, 4). Two assumptions are made: first, that carbon com- ›unds are polar in character, and, secondly, that carbon atoms a chain tend to assume alternately positive and negative arges, and it is shown how, by these assumptions, the alternating aracter of many physical properties in homologous series, for ample, the melting points in the fatty acid series, can be counted for. Further evidence in support of the hypothesis is rived from a consideration of the manner of addition of hydrogen haloids to unsaturated carbon compounds. The electronic formula for propylene, for example, is as annexed; the most hydrogenated carbon atom is electronegative; the adjacent carbon atom is electropositive, and combines with the electronegative



ılogen (Markovnikov's rule). A number of exceptions to this ıle, Ipatiev's rule for the addition of hydrogen bromide to com- ›unds of the type $R_2C{:}C{:}CH_2$, and the isomeric rearrangement alkyl haloids are accounted for by the hypothesis.

E. H. R.

Condensations of n-Butyl Alcohol and n-Butaldehyde. HARLES WEIZMANN and STANLEY FREDERICK GARRARD (T., 1920, 17, 324—338).

The Walden Inversion. II. P. KARRER and W. KAASE *Helv. Chim. Acta*, 1920, **3**, 244—251. Compare A., 1919, 570).—The action of hydrochloric acid on isobutylene oxide sults in the formation of γ-chloro-α-methylpropan-β-ol, accom- ınied by an isomeride, which Michael considered to be β-chloro- methylpropan-γ-ol. There is, however, no positive evidence in vour of this view (Krassusky, A., 1907, i, 459), but confirmation it is now brought forward. *γ-Chloro-βε-dimethylhexan-β-ol*, H_3·CHMe·CH_2·CHCl·CMe_2·OH, obtained by the action of mag- sium methyl iodide on ethyl α-chloro-γ-methylvalerate, is a clear ., b. p. 77°/12 mm., with an odour resembling that of turpentine,

and has $[\alpha]_D^{16}$ $-57\cdot2°$ in alcohol. By treatment with potassium hydroxide, it is converted into $\beta\epsilon$-dimethylhexene-$\beta\gamma$-oxide,

$$CH_3\cdot CHMe\cdot CH_2\cdot \overset{\quad O \quad}{\overbrace{CH\cdot CMe_2}},$$

b. p. 134—136°, $[\alpha]_D^{16}$ $+8\cdot97°$ in alcohol under ordinary pressure, or 46°/17 mm., a clear liquid with a refreshing, fruity odour. It reacts instantly with cold concentrated hydrochloric acid. Although the product boils at 77°/13 mm., and has the same odour as the above chlorodimethylhexanol, it has $[\alpha]_D^{16}$ $+14\cdot15°$ in alcohol, and must therefore contain a certain proportion of the isomeric β-chloro-$\beta\epsilon$-dimethylhexan-γ-ol. The possibility that the production of the mixture is due to a Walden inversion is excluded by the fact that it regenerates the above oxide when treated with potassium hydroxide. The paper concludes with comments on Clough's reply (this vol., i, 368). J. K.

Preparation of Ethylene Glycol. CHEMISCHE FABRIK GRIESHEIM ELEKTRON (D.R.-P. 300122; from *Chem. Zentr.*, 1920, ii, 241).—Ethylene is oxidised with permanganate solution in such a manne that (1) contact of the glycol formed with the permanganate i avoided as far as possible, as, for example, by adoption of th counter-current principle, and (2) accumulation of manganese mu or other products which might retain the glycol in the reactio vessels is obviated. The yields are nearly quantitative. Technica ethylene, such as that obtained by the catalytic hydrogenation o acetylene, and therefore always containing a certain amount o impurities, of which the chief is ethane, may be advantageousl used. The ethane is then obtained as by-product. H. W.

The Preparation of Halogenohydrins. JOHN READ an MARGARET MARY WILLIAMS (T., 1920, **117**, 359—362).

Preparation of Pinacone. FARBENFABRIKEN VORM. FRIEDR BAYER & Co. (D.R.-P. 306304; from *Chem. Zentr.*, 1920, ii, 445) —Acetone is reduced electrolytically in acid solution in th presence of metallic salts, which inhibit its conversion into mor completely reduced products, such as *iso*propyl alcohol. Salts o bismuth, mercury, manganese, nickel, antimony, silver, and iro are found to be particularly suitable for this purpose. H. W.

Preparation of Pinacone Chlorohydrin. FARBENFABRIKE VORM. FRIEDR. BAYER & Co. (D.R.-P. 317635; from *Chem. Zentr* 1920, ii, 445—446).—Hydrogen chloride is allowed to act o pinacone at a temperature which is above that at which th hydrogen chloride additive product is produced, and below that a which pinacolin is formed, or the additive product of pinacon and hydrogen chloride is heated to such a temperature. Pinacon chlorohydrin, a substance with a camphor-like odour, is forme quantitatively at 35—45°. H. W.

Preparation of Ethyl Ether. ELEKTRIZITÄTSWERK LONZA (D.R.-P. 317589; from *Chem. Zentr.*, 1920, ii, 445).—Acetaldehyde vapour is treated with hydrogen in the absence of oxygen and presence of a contact agent.

In previous processes, alcohol has been invariably produced by passing mixtures of acetaldehyde and hydrogen over catalysts (compare this vol., i, 134); apparently, electrolytic hydrogen has been used, which invariably contains oxygen. Only traces of ether are formed from a gaseous mixture containing even a few tenths per cent. of oxygen, whilst, in the complete absence of the latter, mixtures of ether and alcohol are produced which contain up to 15% of the former. The production of ether commences at about 90°, whilst decomposition of the acetaldehyde begins at about 170°; the temperature of the reaction chamber must therefore be maintained between 90° and 170°. H. W.

The Mechanism of the Reaction between Ethylene and Sulphur Chloride. J. B. CONANT, E. B. HARTSHORN, and G. O. RICHARDSON (*J. Amer. Chem. Soc.*, 1920, **42**, 585—595).—The formation of $\beta\beta'$-dichlorodiethyl sulphide by the action of sulphur monochloride on ethylene at 40—60° is the result of two successive reactions, which take place with different velocities. Experiments with carbon tetrachloride and trichlorodiethyl sulphide having confirmed the proportionality of molecular concentration of solute to depression of freezing point of $\beta\beta'$-dichlorodiethyl sulphide, the relationship between ethylene absorption and dichlorodiethyl sulphide formation in the above reaction was determined by the addition of samples of the reaction mixture to such quantities of the pure sulphide as to depress its freezing point from 13·9° to 5—9°. Of the following pairs of figures, the first represents the percentage of sulphide in the reaction mixture when the ethylene absorbed was a percentage of the total eventually absorbed given by the second figure: 0·0, 23·8; 25·5, 45·0; 52·6, 67·25; 70·1, 87·5; 84·9, 100·0. The first stage in the reaction therefore consists in the formation of an intermediate compound, which only reacts further with ethylene when the absorption has reached about 30%; at the stage of 60—70% absorption, the reactions proceed at about the same rate, and later the second predominates completely. An intermediate compound from sulphur dichloride can be isolated in a fairly pure condition (with sulphur and chlorine contents 1% too low and too high, respectively, for the formula $CH_2Cl\cdot CH_2\cdot SCl$) by shaking it at 0° in excess of ethylene. The resulting pale yellow liquid apparently combines with sulphur when warmed with it, because the black, oily product is completely soluble in carbon tetrachloride, and is probably a polysulphide, since by oxidation with nitric acid, sulphuric acid and an unidentified organic sulphonic acid are produced. The intermediate product also evolves hydrogen chloride slowly at 0°, rapidly at 50°, very rapidly in presence of iron or ferric chloride at 5°, and is converted into a viscid, black oil. A similar product, which

behaves very similarly, is present in sulphur monochloride which has absorbed one mol. proportion of ethylene, but the presence of some unchanged monochloride and some dichlorodiethyl sulphide prevents its isolation. Although the ethylene absorbed by sulphur monochloride amounts to 95% of that theoretically required for its complete conversion into the sulphide, only about 80% of this is actually produced, whilst only about 50% of the calculated amount of sulphur is produced (it is not precipitated, but is in colloidal solution, from which it separates slowly at the ordinary temperature and rapidly at 100°, leaving the freezing point of the disulphide unchanged). Correspondingly, a black tar, completely soluble in organic solvents, and so free from elementary sulphur, remains when the sulphide is removed from the final product by distillation under reduced pressure. This tar corresponds approximately in composition with the formula $(CH_2Cl \cdot CH_2)_2S_5$, and, in conformity with this, by oxidation with nitric acid, gives sulphuric acid and a sulphonic acid, probably $CH_2Cl \cdot CH_2 \cdot SO_3H$ (compare Spring, A., 1888, 664). The tar is decomposed by steam at 200°, leaving a black residue rich in sulphur, whilst the steam removes a yellow oil, which boils under reduced pressure with decomposition, and is probably $(CH_2Cl \cdot CH_2)_2S_3$, since, on oxidation, it yields sulphuric acid and a sulphonic acid. That the tar is not a product of decomposition during distillation follows from the fact that its mixture with the requisite amount of pure dichlorodiethyl sulphide has the properties of the original crude product. J. K.

Chloromethyl Chloroformates. André Kling, D. Florentin, A. Lassieur, and R. Schmutz (*Ann. Chim.*, 1920, [ix], **13**, 44—59). —A more detailed account of work already published (compare this vol., i, 8, 139, 213). W. G.

Alcoholysis. II. Alcoholysis in the Absence of a Catalyst. J. J. Sudborough, N. B. Bhagvat, and V. K. Bhagvat (*J. Ind. Inst. Sci.*, 1918, **2**, 121—136).—A study of the alcoholysis in the absence of a catalyst of the methyl and ethyl esters of three pairs of acids, chosen so that each pair were similar in constitution, one being, however, a relatively strong acid and the other relatively weak. The results clearly indicate that esters derived from relatively strong acids enter into double decomposition with monohydric alcohols more readily than do the corresponding esters of weak acids.

Experiments made with methyl dichloroacetate and propyl alcohol confirmed these results, but in this case there was also a certain amount of replacement of the chlorine by the propyl group.

W. G.

Colloid Chemical Studies of Soaps. III. Colloid Chemistry of Potassium Oleate and the Salting-out of Soaps. IV. Reaction of Soaps to Indicators. M. H Fischer and Marion O. Hooker (*Chem. Eng.*, 1919, **27**, 253—257 271—276. Compare this vol., i, 215).—In the first paper the various

theories are discussed that have been proposed to explain the salting out of soaps. The electrolytic theory which attributes the results to the neutralisation of the charge on the particles is inadequate. The authors advance the following. When small amounts of salt are added to a soap–water system the molecules of the former become hydrated and dispersed in the soap–water medium. Further addition of the salt causes not only a greater dehydration of the soap, but also an increase in the viscosity of the system due to the larger proportion of the disperse phase. When sufficient salt has been added the hydrated particles of salt touch one another and a reversal takes place, whereby the largely dehydrated soap becomes the disperse phase. As the density of the dehydrated soap is much less than that of the salt solution the former rises to the top.

In the second paper the contention is raised that a soap made from equivalent amounts of a fatty acid and a standard alkali solution is either acid, neutral, or alkaline toward an indicator, such as phenolphthalein, depending on the concentration of water in the system. A soap–water system may be water dispersed in hydrated soap or hydrated soap dispersed in water. Indicators react with the latter, but not with the former. On heating a soap gel the water may change from the disperse phase to the disperse medium. For this reason the indicator might react with the system at the higher temperature, where it could not do so with the cold gel. These facts must be borne in mind in the application of indicator methods to biochemistry. Living matter is made up of colloids containing water rather than of water containing colloids. It therefore is not always possible to determine by the use of an indicator whether living matter is acid, neutral, or basic. CHEMICAL ABSTRACTS.

β-Alkylthiolcrotonic Esters. HELMUTH SCHEIBLER and JULIUS VOSS (*Ber.*, 1920, **53**, [*B*], 379—388).—A series of β-alkylthiolcrotonic esters has been prepared by the action of sodium alkyl sulphides on the isomeric β-chlorocrotonic esters. In striking contrast to the behaviour of the corresponding free acids, it is found that the normal form is the more stable; isomerisation during the course of the reaction appears to depend not only on the mercaptan used, but also on the particular ester employed.

The β-chlorocrotonic esters are most advantageously prepared (yield, 90—95% of that theoretically possible) by converting the acids into their chlorides by means of thionyl chloride and treating the crude product of the reaction, after removal of excess of thionyl chloride, with the requisite alcohol.

Methyl β-benzylthiolcrotonate, colourless, rhombic leaflets, m. p. 69—70°, is prepared by the action of a methyl-alcoholic solution of sodium benzyl sulphide on methyl chloro*iso*crotonate or methyl chlorocrotonate or from cold methyl alcohol and β-benzylthiolcrotonyl chloride. *Ethyl β-benzylthiolcrotonate*, six-sided plates or rhombic crystals, m. p. 64·5°, is exclusively formed by the action of ethyl β-chlorocrotonate on an alcoholic solution of sodium benzyl-

sulphide; with the corresponding *iso*-ester, however, the main product is *ethyl β-benzylthiolisocrotonate*, viscous, yellow oil, b. p. 204—205°/15 mm., but a small proportion is always converted into the normal ester. Ethyl β-chloro*iso*crotonate yields a mixture of the isomeric *ethyl β-ethylthiolcrotonates*; by fractionation of the product obtained by the action of sodium ethyl sulphide on the mixture of ethyl β-chlorocrotonates it was found possible to isolate the *iso*-ester, b. p. 125—126°/14 mm., 127—129°/16 mm., and 232—236°/ordinary pressure, and the normal ester, b. p. 139—141°/16 mm. H. W.

Metallic Compounds of the Enolic Forms of Carbonyl Compounds and their Application to Syntheses. I. Preparation and Properties of Metallic Compounds of Enolic Forms of Fatty Esters. Action of Ethyl Potassioacetate on Halogenacyl Compounds. HELMUTH SCHEIBLER and JULIUS VOSS (*Ber.*, 1920, **53**, [*B*], 388—409. Compare Scheibler and Babe, A., 1916, i, 14).—The potassio-derivatives of esters which contain at least one hydrogen atom attached to the carbon atom in the α-position to the carbalkyloxy-group are readily obtained when an ethereal solution of the ester is added to the finely-divided metal which is covered with ether heated to gentle ebullition; the metal dissolves immediately with evolution of hydrogen, and the metallic derivative remains more or less completely in colloidal solution in the ether. Sodium acts less energetically, and the corresponding derivatives can frequently be only obtained in boiling benzene or toluene solution, whereby they are partly decomposed. Increase in the weight of the alkyloxy-group appears to facilitate the reaction. The *ester-enolates are very unstable substances, which, however* may be preserved for several days under ether in an atmosphere of hydrogen or nitrogen. Condensation with resulting formation of brown products occurs when their suspensions or solutions in benzene or toluene are warmed, and, on subsequent acidification with dilute mineral acids, acidic products are obtained. They are immediately decomposed by water into ester and alkali hydroxide; addition of alcohol causes the separation of alkyloxide. Dry oxygen is absorbed with formation of brown products. They react with carbon dioxide to give colourless potassium salts of carboxylic acids, which are stable towards oxygen and water, but contain the carboxyl group very loosely combined. They readily undergo addition, condensation, and substitution. Of the various derivatives prepared, ethyl potassio-acetate has been most fully investigated; apart from its mode of formation, the main evidence on which the formula $CH_2{:}C(OK){\cdot}OEt$, proposed for it rests is its action toward ethyl chloroformate. When the substances are brought together in cold *ethereal solution, potassium chloride is immediately precipitated* and the primary, unpleasant-smelling product is decomposed when the solution is boiled, yielding substances with an ester-like odour on *acidification of the solution, carbon dioxide*, ethyl acetate, ethyl

carbonate, and ethyl malonate are obtained, the latter in very small amount. The reactions may be represented by the schemes:

$$2CH_2:C(OEt)\cdot O\cdot CO_2Et \longrightarrow [CH_2:C(OEt)\cdot O]_2CO + Et_2CO_3;$$
$$[CH_2:C(OEt)\cdot O]_2CO + H_2O \longrightarrow 2CH_3\cdot CO_2Et + CO_2;$$
$$[CH_2:C(OEt)\cdot O]_2CO + 2KOH \longrightarrow 2CH_3\cdot CO_2Et + K_2CO_3.$$

The reaction just described offers a certain contrast to that observed by Bouveault and Locquin (A., 1906, i, 782), who, by the action of sodium on solutions of fatty esters in ether or benzene and decomposition of the products with water, obtained ketols; the difference is to be ascribed to the different mode of operation since, in the present instance, the experiments were performed in such a manner that the liberated hydrogen was immediately removed, whilst the French chemists worked at a lower temperature at which the reducing action of the gas could come into operation.

The following individual compounds are described: *ethyl potassioacetate*, pale yellow, amorphous, very hygroscopic powder; *methyl potassioacetate*, pale ochre-yellow; *ethyl sodioacetate*, pale reddish-yellow; *amyl sodioacetate*, yellow; *ethyl potassiopropionate*, pale yellowish-red; *ethyl potassiobutyrate*, yellow, amorphous powder; *ethyl potassiocrotonate*, ochre-coloured powder; *ethyl potassio-β-ethoxycrotonate*; *methyl potassio-β-ethylthiolcrotonate*, yellow powder, which does not absorb dry oxygen; *ethyl potassio-β-ethylthiolcrotonate*, ochre-coloured powder; *ethyl potassio-β-ethylthiolisocrotonate* resembles the preceding substance; *methyl sodio-β-benzylthiolcrotonate*, red powder; *ethyl potossio-β-benzylthiolcrotonate*, yellow; *ethyl sodio-β-benzylthiol*isocrotonate resembles the isomeric compound; *ethyl dipotassio-ββ-thiodicrotonate*, wine-red powder; *ethyl potassiocinnamate*, red powder. Ethyl acetoacetate (1 mol.) and potassium (2 atoms) yield a white product which is readily soluble in ether to a brown solution, but half of the potassium remains unchanged. Ethyl αα-diethylacetoacetate evolves hydrogen when treated with potassium, and yields a yellowish-red, pulverulent, metallic derivative, which is probably formed by enolisation of the β-carbonyl group. Benzoic ester, on the other hand, does not evolve hydrogen when treated with potassium, but slowly gives a black product, which yields acidic substances after being decomposed by water.

The action of acetyl and benzoyl chlorides on ethyl potassioacetate is fundamentally similar to that of ethyl chloroformate. When the solutions are heated, however, various condensation products are formed. The primary product obtained by the use of acetyl chloride is smoothly converted by gaseous ammonia into acetamide and ethyl acetate, $NH_3 + CH_2:C(OEt)\cdot O\cdot COMe = CH_3\cdot CO\cdot NH_2 + CH_2:C(OEt)\cdot OH[\longrightarrow CH_3\cdot CO_2Et]$; when, however, the product is distilled it gives alcohol, ethyl acetate, acetic acid, and acetic anhydride. Similarly, the substance formed when benzoyl chloride is employed yields alcohol, benzoic anhydride, ethyl benzoate, and benzoic acid. Alcohol and acid anhydride appear to be the primary decomposition products from which ester and acid are subsequently

formed. In addition, a highly unsaturated residue with a terpenaceous odour is obtained, which boils over a wide range of temperature and from which it has not been found possible to isolate any individual substance. H. W.

The Walden Inversion. G. W. Clough (*Helv. Chim. Acta*, 1920, **3**, 233—235).—The criticisms of Karrer and Kaase (A., 1919, i, 570) are based on a misconception of the author's views; further, the conclusions as to configuration drawn by Karrer and Kaase from their experimental observations on rotatory dispersion are premature in the present state of knowledge. The author doubts the wisdom of changing the designations of ordinary malic and aspartic acids from *l* to *d*. J. K.

Preparation of Compounds of Deoxycholic Acid. Heinrich Wieland (D.R.-P. 317211; from *Chem. Zentr.*, 1920, ii, 447).—The acid is mixed with a hydrocarbon or other organic compound with the exception of ether and acetic acid.

Choleic acid from bile, which has hitherto been regarded as an isomeride of deoxycholic acid, is an additive product of the latter with fatty acids (palmitic, stearic, and oleic) in the proportion of eight molecules of deoxycholic acid to one molecule of fatty acid. The stable additive products (which are not dissociated in solution) of deoxycholic acid with hydrocarbons, alcohols, phenols, aldehydes, ketones, carboxylic acids, and their esters and alkaloids, which frequently contain the components in definite stoicheiometric relationship, are generally termed choleic acids, so, for example, camphorcholeic acid, phenolcholeic acid, etc. *Stearincholeic acid*, m. p. 186°, is prepared from deoxycholic acid and stearic acid dissolved in alcohol. *Naphthalenecholeic acid* [naphthalene (1 mol.) and deoxycholic acid (3 mols.)] has m. p. 182°. The choleic acids which are freely soluble in alcohol are prepared by dissolving deoxycholic acid in the molten component, allowing the product to crystallise, and removing the excess of the second component by a suitable solvent. *Phenolcholeic acid* crystallises from a small quantity of alcohol, is odourless, and yields sparingly soluble *calcium* and *barium* salts. *Benzaldehydecholeic acid*, from benzaldehyde (1 mol.) and deoxycholic acid (3 mols.), has m. p. 168°. The products are expected to find application in pharmacy. H. W.

The Enolisation of Carbonyl Compounds under the Influence of Grignard's Reagents. Vinayak Keshav Bhagvat and J. J. Sudborough (*J. Ind. Inst. Sci.*, 1919, **2**, 187—194).—Using the method described by Hibbert and Sudborough (T., 1904, **85**, 936) for the estimation of hydroxyl groups in carbon compounds by measuring the volume of methane produced by contact with an excess of magnesium methyl iodide solution, the authors have determined the enolisation produced in a number of aldehydes, ketones, and β-ketonic esters by contact with Grignard's reagents.

The results indicate that the carbonyl group in aldehydes and ketones is only enolised to a small extent, 11% being the maximum, under these conditions. In β-diketones and β-ketonic esters, how-

ever, the carbonyl group shows a very great tendency to undergo enolisation. In the case of benzoyl- and acetyl-acetone as much as 90% of the enolic form is produced. W. G.

The Vapour Pressures of Acetone. G. R. PARANJPÉ (*J. Ind. Inst. Sci.*, 1918, **2**, 47—58).—Using the statical method, the author has measured the vapour pressures of acetone over the temperature range $-50°$ to $15°$ for a sample of fermentation acetone, D_{25}^{25} 0·7909, and for a sample of commercial "extra pure" acetone, D_{25}^{25} 0·7865. W. G.

Biochemical Synthesis of some Disaccharides: Glucobioses, Galactobioses. ÉMILE BOURQUELOT (*Ann. Chim.*, 1920, [ix], **13**, 5—44).—A full account of work already published (compare A., 1913, i, 1080, 1305; 1914, i, 72, 499, 662; 1915, i, 76, 501, 940; 1916, i, 596; 1917, i, 250; 1919, i, 137, 361). W. G.

Occurrence of Melezitose in Honey. C. S. HUDSON and S. F. SHERWOOD (*J. Amer. Chem. Soc.*, 1920, **42**, 116—125).—The occurrence of melezitose in manna from the Douglas fir of British Columbia has recently been reported (A., 1919, i, 59); the same sugar has now been found in several samples of honey. In estimating the percentage of melezitose, advantage is taken of the fact that invertase hydrolyses sucrose, but not melezitose; the change in rotation after treatment with invertase and acid, respectively, is therefore determined, or, alternatively, the reducing power may be measured after similar treatment. H. W.

Crystallography of Melezitose. EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1920, **42**, 125—128).—The crystals of melezitose dihydrate belong to the rhombic system, and are seemingly holohedral, but no doubt bisphenoidal, $a:b:c=1{\cdot}216:1:0{\cdot}496$. Under the microscope, melezitose presents the form of plates and rods, in part rectangular in outline and in part terminated by faces inclined at large angles. The habit and the weak double refraction are useful in the identification of this sugar in honeys or honey dews; the dextrose which frequently separates from honeys is in rods terminated at one end by planes lying 60° apart, and rounded at the other end, and in parallel polarised light shows, at least in the centres of the grains, brilliant colours of the second order with − elongation. Sucrose can also be readily distinguished from melezitose by its much greater double refraction, α being 1·45 and γ 1·57, and by breaking into irregular fragments with oblique extinction. The refractive indices for melezitose for different wave-lengths are given in the appended table.

	Wave-length.					
Index.	450.	500.	550.	D 589.	600.	650.
α	1·550	1·546	1·542	1·540	1·540−	1·538
β	1·558	1·553	1·550	1·548	1·547	1·545
γ	1·561	1·556	1·552	1·550	1·549	1·547
$\gamma-\alpha$	0·011	0·010	0·010	0·010	0·009+	0·009

H. W.

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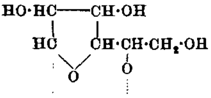
Glucosides. VI. Constitution and Configuration of Glucosides. P. KARRER (*Helv. Chim. Acta*, 1920, **3**, 258—260).—Pictet has been led by his observation that the lævoglucosan obtained by distillation of starch and cellulose (A., 1918, i, 59) can be similarly obtained from a number of glucosides (this vol., i, 66) to suggest that the γ-oxide formula for glucosides should be modified. Since, however, he also found that ordinary α-glucose only yielded traces of the lævoglucosan, and the glucosides he examined were all β-compounds, it appeared to the author that spatial configuration might be the determining factor in the reaction. He *confirmed* this hypothesis by showing that a considerable amount of lævoglucosan is obtainable from β-glucose. Perhaps, therefore, starch and cellulose contain β-glucosidic linkings; it is possible that they contain the lævoglucosan grouping, but not necessarily so. The structure of the trimethylglucose obtained from cellulose (Denham and Woodhouse, T., 1917, 244) suggests that the glucose residues in cellulose are coupled at the points indicated (see annexed constitution).



J. K.

The Substitution of Halogens for the Amino-group in Aliphatic Amines. CHEMISCHE FABRIK FLORA (Brit. Pat. 132245).—The amino-groups of aliphatic amines may be replaced by chlorine or bromine by treatment at 50—100° with a mixture of nitric acid (D 1·4) and concentrated hydrochloric or hydrobromic acid respectively. The reaction, which from the technical point of view is particularly applicable to the amino-acids, such as leucine or aspartic acid, is accompanied by vigorous evolution of nitrogen, and proceeds without appreciable formation of by-products. Instead of using a mixture of the two acids, nitric acid may be used with a chloride or bromide, or the halogen acid with a nitrate.

G. F. M.

Preparation, Crystallography, and Optical Properties of Methyl- and Ethyl-ammonium Mercuri-iodides. GEORGE S. JAMIESON and EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1920, **42**, 136—145).—It has been found recently by Woodward and Alsberg (unpublished work) that minute quantities of tertiary methyl- and ethyl-amines can be precipitated and detected by Mayer's reagent in the presence of primary and secondary amines provided only small quantities of the latter are present; with larger quantities, however, the latter substances also give precipitates, which are now described. All the substituted ammonium mercuri-iodides are bright yellow in colour, and are decomposed by water, *with the separation of red mercuric iodide. They all* dissolve readily in an excess of potassium iodide, and care is there-

ore necessary in the preparation of Mayer's reagent, which is made y dissolving exactly 45 grams of mercuric iodide and 33 grams f potassium iodide so as to make 100 c.c. of solution.

Dimethylammonium mercuri-iodide, $NH_2Me_2HgI_3$, m. p. 122°, *rimethylammonium mercuri-iodide*, m. p. 136°, *diethylammonium nercuri-iodide*, m. p. 114°, and *triethylammonium mercuri-iodide*, n. p. 77—78° or 59—60°, according to the mode of preparation, re described. Dimethylamine and diethylamine cannot be etected in this manner if present in amounts less than 20 and mg. per c.c. respectively.

The refractive indices of the compounds are extremely high (1·9 o 2·0), but cannot be accurately determined by the immersion ethod, since these substances are decomposed more or less rapidly y all suitable liquids. The following crystallographic data are ecorded: dimethylammonium mercuri-iodide, monoclinic, domatic, $:b:c=0·9687:1:1·3406$, $\beta=78°20'$; diethylammonium mercuri-odide, rhombic, peri-cubic, $a:b:c=1·1572:1:0·9102$; trimethyl-mmonium mercuri-iodide, rhombic, peri-hexagonal, $a:b:c=$ ·7262 : 1 : 0·9569; triethylammonium mercuri-iodide, monoclinic, eri-tetragonal, $a:b:c=1·15:1:1·08$, $\beta=62°30'$; tetramethyl-mmonium mercuri-iodide, rhombic, peri-hexagonal, $a:b:c=$ ·59 : 1 : 0·52; tetraethylammonium mercuri-iodide, tetragonal, $:c=1:1·1577$. H. W.

The Stereochemistry of the Platinum Atom; on Re-tively Asymmetric Syntheses in Inorganic Complexes. LEXANDER P. SMIRNOV (*Helv. Chim. Acta*, 1920, **3**, 177—195). -Werner has described the preparation and resolution into optic-ly active components of the compounds $[Pt\,en_3]X_4$ (*Vierteljahrs-hrift Naturf. Ges. Zürich*, 1917, **62**, 553), and the author now escribes similar experiments with the salts $[Pt\,pn_3]X_4$ (pn = ropylenediamine). No isomerism conditioned by the *cis*- or *ans*-positions of the methyl groups was observed when either the cemic or one of the active forms of the diamine were used; all ree series of salts closely resembled those derived from ethylene-amine, hut their solubility, especially when the active forms were esent, was much greater, and this at first prevented the resolu-on of the inactive forms. The molecular rotations of the salts rived from each of the active forms of diamine are remarkably gh aud of equal value, but of opposite sign, this being the same those of the diamines themselves; for example, $[M]_D$ for

$$D_D-[Pt\ d\text{-}pn_3]Cl_4,1H_2O$$

d for $L_D-[Pt\ l\text{-}pn_3]Cl_4,1H_2O$ = 1035° and −1013° respectively therefore seemed possible that the members of one series were e optical antipodes of those of the other, and this was confirmed a consideration of the molecular rotations of the plati-com-unds containing either one or two molecules of propylenediamine 'schugaev and Sokolov, A., 1909, i, 137). From these it appears at the presence of each molecule of propylenediamine carries th it a rotation of 96°. In the above instances, the observed

rotation is very much in excess of 288°, the value calculated on the basis of three molecules of diamine, and the difference represents the rotation due to the asymmetry of the complexes themselves. This difference, however, is considerably greater than that observed by Werner for the rotation of the optically active ethylenediamine salts, owing to the influence of the methyl groups. As the salts are colourless, they show no absorption in the visible spectrum or anomalous curve of rotatory dispersion, and no confirmation of the above conclusions is obtainable on optical grounds, but these are available in the case of the corresponding cobalt compounds. Thus, a comparison of the curves of molecular rotatory dispersion of $D_D-[Co\ d\text{-}pn_3]Br_3,2H_2O$ and

$$L_D-[Co\ l\text{-}pn_3]Br_3,2H_2O$$

with those of d_D and $l_D-[Co\,en_3]Br_3,2H_2O$ shows that they have the same form, with points of inversion, respectively, at $\mu\mu$ 503·5 and 492, and maxima (or minima, as the case may be) in the region $\mu\mu$ 517—527. The values for the ethylenediamine salts are throughout numerically greater than those for the propylenediamine compounds, because these are composite values representing the effect of the active complexes and that of the active propylenediamine. The latter is always opposite in sign to the rotation of the free propylenediamine (Tschugaev and Sokolov), and, as a consequence, in the region where the values for the ethylenediamine derivatives show that the effect of the complex is scarcely perceptible, a second reversal of sign takes place at $\mu\mu$ 626. Finally, the product which separated when a solution containing $[Pt\,r.\text{-}pn_3](d\text{-}C_4H_4O_6)_2$ was nucleated with

$$L_D-[Pt\,d\text{-}pn_3](d\text{-}C_4H_4O_6)_2,H_2O$$

was identical with this compound, and

$$D_D-[Pt\,l\text{-}pn_3](d\text{-}C_4H_4O_6)_2,H_2O$$

was obtained from the residual solution after treatment with potassium chloride.

In both cases, therefore, a total asymmetric synthesis has been effected, which is parallel to the formation of one rhamnohexonic acid and one mannoheptonic acid only from rhamnose and mannose (*E. Fischer and others*, A., 1888, 1049; 1889, 480). This phenomenon therefore extends to atoms with other spatial relationships than that of the tetrahedral carbon atom, and the internal spatial configuration of molecules associated with a central atom determines the spatial relationship of such molecules to that atom.

r.-*Platinum tripropylenediamine tetrachloride*,

$$[Pt\,pn_3]Cl_4,H_2O,$$

prepared by heating an alcoholic solution of chloroplatinic acid at 100° with r.-propylenediamine hydrochloride, forms a white granular, crystalline powder after crystallisation from dilute alcohol; the *bromide*, r.-$[Pt\,pn_3]Br_4$, from the chloride by double decomposition with sodium bromide, is a yellowish-white, crystalline powder; the *iodide*, r.-$[Pt\,pn_3]I_4$, from the chloride and ammonium iodide, is orange-yellow, but blackens even in the dark

the *sulphate*, *r.*-[Pt pn_3]$(SO_4)_2$, and the *nitrate*, *r.*-[Pt pn_3]$(NO_3)_4$, are obtained from the chloride and the corresponding silver salts.

l-*Platinum tripropylenediamine tetrachloride*,

L_D − [Pt *d*-pn_3]Cl_4,H_2O,

prepared from *d*-propylenediamine, has $[M]_C$ − 844°, $[M]_D$ − 1013°, $[M]_E$ − 1419° in 0·5% aqueous solution. The *bromide*,

L_D − [Pt *d*-pn$)_3$$Br_4$,

iodide, L_D − [Pt *d*-pn_3]I_4, and *tartrate*,

L_D − [Pt *d*-pn_3]$(d\text{-}C_4H_4O_6)_2$,H_2O,

give very similar values for their molecular rotations.

d-*Platinum tripropylenediamine tetrachloride*,

D_D − [Pt *l*-pn_3]Cl_4,H_2O,

has $[M]_C$ + 839°, $[M]_D$ + 1035°, $[M]_E$ + 1413° in 0·5% aqueous solution; the *bromide*, D_D − [Pt *l*-pn_3]Br_4, *iodide*, D_D − [Pt *l*-pn_3]I_4, and *tartrate*, D_D − [Pt *l*-pn_3]$(l\text{-}C_4H_4O_6)_2$,H_2O, were also prepared.

The chloride and bromide of each of the last two series, obtained by resolution of the salts of the racemic series, agreed in their properties with the above description. From the chlorides, the respective active forms of propylenediamine were obtained by decomposition at 100° with formaldehyde solution.

Salts of the tri-*l*-propylenediaminecobalti-series have already been described (Tschugaev and Sokolov). Tri-*d*-propylenediaminecobalt bromide, D_D[Co *d*-pn_3]Br_3,$2H_2O$, was prepared by heating *d*-propylenediamine with chloropentamminecobalt chloride, or 1:6-dichlorotetrapyridinecobalt chloride, or 1:6-dichlorodipropylenediaminecobalt chloride; the solution of the chloride thus obtained being treated with sodium bromide. Details are given of the values for the molecular rotations with various wave-lengths, from which the curves described above were constructed.

J. K.

Preparation of Hexamethylenetetramine. A. Sander (*Zeitsch. angew. Chem.*, 1920, **33**, 84).—The author disputes Herzog's contention (this vol., i, 292) that the formation of hexamethylenetetramine by treatment in the cold of an ammonium salt with excess of formaldehyde is confined to the carbonate. The reaction also takes place with other ammonium salts, and may be utilised for their estimation. Ammonium carbonate, however, more readily yields a pure product than other salts. W. J. W.

Synthesis of a Peptide of Aspartic Acid by means of Vegetable Enzymes. C. Ravenna (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 55—58).—Treatment of aqueous asparagine solution with pulped spinach leaves in presence of toluene for twenty days at about 25° appears to result in the formation of the dipeptide of aspartic acid, asparagylaspartic acid (compare this vol., i, 150, 151) in small proportion. Further experiments on a large scale are in progress. T. H. P.

Compounds of Thiocyanates of certain Bivalent Metals and Hydrazine. PRIYADARANJAN RÂY and PULIN VIHARI SARKAR (T., 1920, 117, 321—323).

Chromic Thiocyanates. NIELS BJERRUM (*Det. K. Danske. Vidensk. Selskabs Skrifter, Nat. Math.*, 1915, 7, pp. 66; from *Chem. Zentr.*, 1920, i, 414—415).—A full account is given of the complex chromic thiocyanates and their equilibrium.

Tervalent chromium yields the following complex ions with H_2O and CNS (CNS = X), in which the water is replaced step by step by the CNS radicle: $Cr\,aq_6^{+++}$, $Cr\,aq_5\,X^{++}$, $Cr\,aq_4\,X_2^{+}$, $Cr\,aq_3\,X_3$, $Cr\,aq_2\,X_4^{-}$, $Cr\,aq\,X_5^{--}$, and $Cr\,X_6^{---}$. The substance, $Cr\,aq_3\,X_3$, is a non-electrolyte. The existence of the second and third complexes could be established in solution, but the corresponding substances could not be isolated in the solid state; they are insoluble in ether. *Trithiocyanotriaquochromium* could be obtained in the crystalline condition, but not in a state of purity; in solution, it can be prepared in a much purer form. The molecular conductivity of a 0·1*N*-solution of the crystals is $\mu = 3{\cdot}87$ at 0°, whilst, under similar conditions, the value $\mu = 250$—300 is in general observed for a tervalent electrolyte. When dried in a vacuum, the very hygroscopic crystals retain 3·2—3·6 H_2O, which is obviously chemically combined in the complex. The *tetrathiocyano*-complex could be obtained in the form of a dilute solution of the free acid, from which the corresponding salts were prepared, but could not be isolated in the solid state. Quinine and strychnine yielded precipitates of varying composition; quinoline salts gave an oily precipitate. The free acid is freely soluble in ether, in which the salts do not dissolve. The *pentathiocyano*-complex was isolated as the beautifully crystalline *quinoline* salt, from which the free *acid* and the *sodium* salt were prepared. It contains $1H_2O$ in complex union; the free acid is soluble in ether, but the salts are not. The *quinoline* salt (which does not contain water of constitution) and the *pyridine* salt of the hexathiocyano-complex are described. All the chromothiocyano-complexes give reddish-violet solutions in water, the shade becoming more red and deeper with increasing CNS content.

For the soluble complexes the partition-coefficient between ether and water at the ordinary temperature is: $Cr\,aq_3\,X_3$, *ca.* 3·6; $H[Cr\,aq_2\,X_4]$, *ca.* 9·4; $H_2[Cr\,aq\,X_5]$, ca. 4; $H_3[CrX_6]$, *ca.* 0·3. In the cases of the tri- and tetra-thiocyano-complexes the values for the partition-coefficient depend somewhat on the mode of preparation of the compounds, which probably points to the presence of mixtures of stereoisomerides, such as are to be expected from Werner's theory.

The velocity of decomposition of the several complexes has been measured by estimating the concentration of the CNS ions by the coloration with ferric nitrate. In aqueous solution, the stability of the hexathiocyano-complex is almost independent of the reaction of the solution. The remaining complexes become more stable in

acid solution as their CNS content diminishes, whilst the reverse is the case in alkaline solution. The trithiocyano-complex is fairly stable in ethereal solution, in which the stability of the other complexes rapidly diminishes with the CNS content. The complexes are sensitive to light.

Analytical methods for the estimation of the several complexes have been worked out. The hexa- and penta-complexes are first precipitated as quinoline salts, and their relative proportions in the precipitate are elucidated by estimation of the Cr and CNS content. The tri and tetra-complexes are removed from the filtrate by means of ether when it is found possible to separate them by fractionation and to determine their amounts by two chromium estimations. Finally, chromium and thiocyanogen are titrimetrically estimated in the extracted aqueous solution, and the content of mono- and di-complex can then be calculated if the content of hexa-aquo-complex is known. The latter is determined by precipitation as chrome alum with potassium hydrogen sulphate and alcohol.

The chromothiocyano-complexes are slowly formed in solutions which contain the hexa-aquochrome-ion and the CNS ion. At the ordinary temperature, however, the stable state is not attained for some years. The chemical equilibrium between the various complexes and the CNS ion has been determined in aqueous solution at 50° for ten solutions. The results of chemical analysis are confirmed by measurements of the electrolytic conductivity. The affinity of the chromium atom for the CNS ion in normal solution is calculated from the equilibrium constants in the usual manner, and is found to be +3710 cal. for the first and −570 cal. for the last CNS group.

Graphs are given showing the relationship between the complexity and the concentration of the CNS ion, from which the equilibrium in a solution can be calculated if the concentrations of Cr and CNS are known. H. W.

The Thiocyanates of Gold and Free Thiocyanogen. Gold Chloride. NIELS BJERRUM and AAGE KIRSCHNER (*Det. K. Danske Vidensk. Selskabs Skrifter, Nat. Math.*, 1918, **6**, pp. 76; from *Chem. Zentr.*, 1920, i, 415—417).—The thiocyanates of gold have been investigated, since they are representatives of very complex and somewhat unstable salts, and permit the examination of the different stages of oxidation of a metal. The behaviour of aurithiocyanates leads to the assumption of the existence of free thiocyanogen in solution.

Potassium aurithiocyanate, $KAuX_4$ (X = CNS), is very sparingly soluble in water, the solubility product being 6×10^{-5} in 1·4 ionic normal solution. *Ammonium aurithiocyanate*, NH_4AuX_4, is a reddish-yellow substance prepared by the precipitation of an aqueous solution of ammonium thiocyanate with a solution of auric chloride (0·4% Au) in hydrochloric acid. *Sodium aurithiocyanate* forms ruby-red needles, solubility product 5×10^{-4} in 2·2 ionic-normal solution. *Hydrogen aurithiocyanate*, $HAuX_4,2H_2O$, forms dark red crystals and is prepared by mixing an acidified solution of

sodium thiocyanate with chloroauric acid and extracting the solution with ether. In pure solution, the aurithiocyanate is mainly present as the ion, AuX_4^-, the complexity constant of which,

$$K_X = AuX_4/Au^{+++} \times X^{-4},$$

is $10^{17 \cdot 7}$ times as great as that of the $AuCl_4$ ion. It is dark reddish-brown in colour, and at $\lambda = 578\ \mu\mu$ has a molar extraction-coefficient, 108. When the concentration of the thiocyano-ion is greater than 0·2, penta- and hexa-thiocyanoauri-ions are present in considerable amount, the complexity constants of which are $K_{AuX_5} = AuX_5^{=}/AuX_4 \times X = 1 \cdot 0$ and $K_{AuX_6} = AuX_6^{=}/AuRh_5^{=} \times Rh = 1 \cdot 1$. The colour is darker than that of the tetra-complex, whilst the molar extinction-coefficient for the penta-complex is about 218 and for the hexa-complex about 248 for $\lambda = 578\ \mu\mu$. At low concentrations of the thiocyanogen and hydrogen ions, the tetra-complex appears to undergo hydrolysis according to the scheme $AuX_4^- + H_2O = AuX_3(OH)^- + H^+ + X^-$, but even when H^+ and $Rh^- = 0 \cdot 01$ scarcely more than 20% is thus decomposed. The tetrathiocyanoauri-ion is dissociated into dithiocyanoauri-ion and free thiocyanogen, $AuX_4^- = AuX_2^- + X_2$, the latter functioning as a colourless, composite halogen, the activity of which lies between those of bromine and iodine; it is liberated from thiocyanates by bromine, but immediately displaces iodine from iodides. It is extremely unstable and rapidly undergoes hydrolysis in aqueous solution, $3(CNS)_2 + 4H_2O = 5H^+ + 5(CNS)^- + HCN + H_2SO_4$; this final result is due to four partial processes: (1) $(CNS)_2 + H_2O \rightleftharpoons H^+ + CNS^- + H(CNS)O$; (2) $2H(CNS)O \longrightarrow H^+ + CNS^- + H(CNS)O_2$; (3) $H(CNS)O + H(CNS)O_2 \longrightarrow H^+ + (CNS)^- + H(CNS)O_3$; (4) $H(CNS)O_3 + H_2O \longrightarrow HCN + H_2SO_4$. The velocity of reaction is conditioned by the slow rate of the second process, for which the following equation is valid: $d[X_2]/dt = -k'[HXO]^2 = -KX^2/[H^+]^2 \times [X^-]^2$, k being about 5 at 18°.

Hydrogen aurothiocyanate, $HAuX_2$, is prepared as an unstable oil by the reduction of hydrogen aurithiocyanate with sulphite, acidification of the solution, and extraction with ether. The corresponding *potassium* salt consists of slender, colourless needles readily soluble in alcohol, but decomposed by water. The *ammonium* salt is colourless and crystalline. The complexity constant of the AuX_2^- ion, which is present in the aqueous solution of these salts, is $10^{22 \cdot 4}$ times smaller than that of the corresponding cyanogen ion. *Monamminoaurothiocyanate*, $AuNH_3X$, from ammonia and dithiocyanoauro-salts in reversible reaction, is unstable and sensitive to light.

Aurithiocyanate may be estimated in the presence of aurothiocyanate by titration with sulphite until a colourless solution results, since the latter ion is colourless. In solution, aurithiocyanate is converted into aurothiocyanate by auto-reduction in accordance with the scheme: $3AuX_4^- + 4H_2O = 3AuX_2^- + 5H^+ + 5X^- + HCN + H_2SO_4$; the presence of hydrogen and thiocyanogen ions and of aurothiocyanate retards this action, which is caused by the instability of free thiocyanogen liberated owing to dissociation of

the aurithiocyanate. The rate of reaction can be calculated from the dissociation constant of aurithiocyanate and the velocity of decomposition of thiocyanogen. A solution of aurothiocyanate dissociates into gold and aurithiocyanate: $3AuX_2^- = 2Au + AuX_4^- + 2X^-$, the equilibrium constant of which is *ca.* 33. The rate of reciprocal action increases with decreasing concentration of H- and CNS-ions. The presence of gold powder catalyses the change. The conjoint effect of auto-reduction and precipitation of gold is that solutions of gold thiocyanate gradually deposit the whole of the metal.

In hydrochloric acid solution the gold of chloroauric acid is mainly present in the form of the ion, $AuCl_4^-$, which, in pure solution, is hydrolysed as follows: $AuCl_4^- + H_2O = AuCl_3(OH)^- + H^+ + Cl^-$. The equilibrium constant is $0{\cdot}55 \times 10^{-4}$.

The authors have estimated the following normal potentials at about 18° ($X = CNS$): (1) $Au + 2X^- = AuX_2^- + \ominus$, 0·689 volt; (2) $AuX_2^- + 2Rh^- = AuX_4^- + 2\ominus$, 0·645 volt; (3) $Au + 4X^- = AuX_4^- + 3\ominus$, 0·660 volt; (4) $Au + 4Cl^- = AuCl_4^- + 3\ominus$, 1·001 volt; (5) $2X^- = X_2 + 2\ominus$, 0·769 volt. The value given by Abegg and Campbell for the normal potential of the gold auro-ion is untrustworthy, since when measurements of the gold electrode potential ion in concentrated nitric acid solution saturated with aurous oxide are made, it is, in reality, the oxidation potential of the nitric acid which is determined. H. W.

Isomerisation and Polymerisation of Methyl Thiocyanate. J. GILLIS (*Rec. trav. Chim.*, 1920, **39**, 330—338. Compare A., 1918, i, 157).—By repeating Walden's work (compare A., 1906, ii, 336) it was found that, at 130°, the influence of different dissolved substances was variable. Except with cadmium iodide and sulphuric acid, the catalytic effect in causing isomerisation and polymerisation is a minimum. Methyl thiocyanate undergoes appreciable isomerisation at 130°, and polymerisation is also noticeable. The ebullioscopic constant of methylthiocarbimide is in agreement with the constant deduced from Trouton's law.

A study of the influence of temperature shows that isomerisation is practically a complete reaction, but it is always accompanied by some polymerisation. Foreign substances introduced into the methyl thiocyanate may have differing catalytic effects on the isomerisation and on the polymerisation. Thus cadmium iodide accelerates the former and sulphuric acid the latter. W. G.

New Method of Formation of Nitriles by Catalysis. A. MAILHE (*Compt. rend.*, 1920, **170**, 813—815).—Aliphatic or aromatic nitriles may be prepared by passing the vapours of the corresponding esters, along with ammonia, over aluminium oxide or thorium oxide at 500° (compare A., 1918, i, 105). It is now shown that the ammonia may be replaced by the vapours of primary amines, the action being $R{\cdot}CO_2Et + C_nH_{2n+1}{\cdot}NH_2 = R{\cdot}CN + EtOH + H_2O + C_nH_{2n}$. In some cases, slight secondary actions occur. W. G.

Preparation of Unsaturated Nitriles by Catalysis. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1920, [iv], **27**, 226—229).—The method of preparation of aliphatic or aromatic nitriles, by passing the vapours of the esters of the corresponding acids, along with ammonia, over aluminium oxide at 480—500° (compare preceding abstract), can be applied to the preparation of unsaturated nitriles, such as crotononitrile, oleonitrile, elaïdonitrile, and cinnamonitrile. W. G.

An Isomeride of Potassium Ferricyanide. II. I. BELLUCCI (*Gazzetta*, 1920, **50**, i, 23—29).—Hauser and Biesalski's statement (A., 1913, i, 26) that the green isomeride of potassium ferricyanide, described by Locke and Edwards (A., 1899, i, 407, 557), and studied by Bellucci and Sabatini (A., 1911, i, 430), Piutti (A., 1912, ii, 712), and Wells (A., 1913, i, 347), consists of the red ferricyanide contaminated with a trace of Prussian-blue, is denied.
T. H. P.

Observations on some Organic Compounds of Arsenic. ALEX. MCKENZIE and JOHN KERFOOT WOOD (T., 1920, **117**, 406—415).

Influence of Position on the Boiling Points of Isomeric Benzene Derivatives. NEVIL VINCENT SIDGWICK (T., 1920, **117**, 389—395).

Some Derivatives of *p*-Dichlorobenzene. JOYCE H. CROWELL and L. CHAS. RAIFORD (*J. Amer. Chem. Soc.*, 1920, **42**, 145—152).—The investigation was undertaken with the object of finding a method of utilising the considerable amounts of *p*-dichlorobenzene which are formed as by-products in the technical production of chlorobenzene.

p-Dichlorobenzenesulphonic acid is most conveniently prepared (yield, 85—90%) by heating *p*-dichlorobenzene with sulphuric acid containing 10—12% of sulphur trioxide at 140—150°; 2:2′:5:5′-*tetrachlorodiphenylsulphone*, colourless, diamond-shaped crystals, m. p. 179°, is also formed. 2:5-Dichloro-4-nitrobenzene cannot be conveniently sulphonated, since reaction does not occur below 150°, whilst, above this temperature, violent decomposition with almost complete decomposition occurs. 2:5-*Dichloro-4-nitrobenzenesulphonic acid*, flat, yellow, very hygroscopic needles, m. p. about 150°, can, however, be obtained by the action of fuming nitric acid (D 1·6) alone or in the presence of concentrated sulphuric acid on *p*-dichlorobenzenesulphonic acid (the *sodium*, *potassium*, *ammonium*, and *barium* salts are described). The constitution of the acid is deduced from the reduction of its sodium salt to the corresponding *amino*-compound (the *acetyl* derivative of which was prepared) and oxidation of the latter to 2:5-dichlorobenzoquinone. Reduction of an alkaline or faintly acid solution of the sodium salt of the nitrosulphonic acid yielded *sodium* 2:2′:5:5′-*tetrachloroazobenzene-4:4′-disulphonate*. H. W.

Benzenesulphonitroamide, Toluene-4-sulphonitroamide, 2-Nitrotoluene-4-sulphonitroamide and some of their Salts. BRUCE REID MATTHEWS (*J. Physical Chem.*, 1920, **24**, 108—119).—A number of metallic salts of benzenesulphonitroamide, toluene-4-sulphonitroamide, and 2-nitrotoluene-4-sulphonitroamide have been prepared and described. *Ammonium benzenesulphonitroamide*, $C_6H_5\cdot SO_2\cdot N(NO_2)\cdot NH_4$, is formed by neutralising the free nitroamide with aqueous ammonia, and forms fine, yellow prisms; the corresponding *sodium*, colourless crystals; *calcium*, *barium*, *strontium*, *lithium*, *silver*, *copper*, and *nickel* salts are described, and also deep blue needles of the composition

$$(C_6H_5\cdot SO_2\cdot N\cdot NO_2)_2Cu,4NH_3.$$

Strychnine benzenesulphonitroamide, $C_6H_5\cdot SO_2\cdot N_2O_2H.C_{21}H_{22}N_2O_2$, is precipitated on adding strychnine nitrate to a hot aqueous solution of the ammonium salt.

Nitration of *p*-toluenesulphonamide with nitric acid (D 1·42—1·48) gives a mixture of p-*toluenesulphonnitroamide*, $C_6H_4Me\cdot SO_2\cdot NH\cdot NO_2$, and 2-nitrotoluene-4-sulphonitroamide, from which the former is extracted with ether; the residue obtained on evaporation of the ethereal solution, when recrystallised from toluene, gave a colourless, crystalline product, m. p. 110°. The *ammonium*, *potassium*, *barium*, *silver*, and *copper* salts are described. When silver oxide is added to an aqueous solution of the nitroamide, grey-coloured needles of the composition $C_6H_4Me\cdot SO_2\cdot NAg\cdot NO_2,2NH_3$, and a similar *copper* compound, $(C_6H_4Me\cdot SO_2\cdot N[NO_2])_2Cu,4NH_3$, can be prepared. *2-Nitrotoluene-4-sulphonitroamide*, $NO_2\cdot C_6H_3Me\cdot SO_2\cdot NH\cdot NO_2$, is obtained in the process described; nitric acid (D 1·48—1·50) being employed. It forms pale yellow needles, m. p. 118·5°. The *potassium*, *copper*, *silver*, *nickel*, and *manganese* salts are described, and also *silver* and *copper* salts containing $2NH_3$ and $5NH_3$ respectively. Practically all the salts described are very soluble in liquid ammonia.

J. F. S.

Preparation of αβ-Dibromotetrahydronaphthalene and of Δ¹-Dihydronaphthalene. JULIUS VON BRAUN (D.R.-P., 316218; from *Chem. Zentr.*, 1920, ii, 241).—Tetrahydronaphthalene is treated with the calculated quantity of bromine at 100—140°, and the dibromotetrahydronaphthalene so produced is treated, if desired, with magnesium (1 atom) in the presence of ether or with tin (rather more than 1 atom) in the presence of alcohol. *αβ-Dibromotetrahydronaphthalene* has m. p. 69°; *Δ¹-dihydronaphthalene* has b. p. 85°/15 mm., m. p. −8°, a_D^{20} 0·9963, and is quantitatively transformed by bromine into the dibromide.

H. W.

Some Nitro-derivatives of Dimethylaniline. J. SMIT (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 523—525).—In the nitration of 3:4-dinitrodimethylaniline, if the nitric acid contains much nitrous acid, or if the action proceeds for a long time, or if the temperature rises above 20°, nitroso-compounds are obtained

as well as 3 : 4 : 6- and 2 : 3 : 4-trinitrodimethylanilines. The author has isolated 3 : 4-*dinitrophenylmethylnitrosoamine*, m. p. 108—109°, and 3 : 4 : 6-*trinitrophenylmethylnitrosoamine*, m. p. 201°.

By the nitration of 3 : 6-dinitrodimethylaniline, in addition to the 3 : 4 : 6-trinitro-derivative, a small amount of 3 : 6-*dinitrophenylmethylnitrosoamine*, m. p. 132°, is obtained. In this nitration, the effect of nitrous acid on the reaction velocity is very great, and if the temperature of the reaction is perceptibly higher than the ordinary temperature, the only final product is 3 : 4 : 6-trinitrophenylmethylnitrosoamine. W. G.

Catalytic Decomposition of Schiff's Bases. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1920, [iv], **27**, 229—234. Compare A., 1919, i, 395).—When Schiff's bases are passed alone over reduced nickel at 420—430°, a change first occurs which is similar to that which was found to occur during the catalytic hydrogenation (*loc. cit.*), $RCH{:}NR' + 2H_2 = R{\cdot}CH_3 + R'NH_2$, the hydrogen being formed by the partial destruction of the group $R{\cdot}CH{:}$. In the second place, nitriles were formed, thus: $RCH{:}NR' = RCN + R'H$, this being, however, the less important change. W. G.

The Constitution of Capsaicin, the Pungent Principle of Capsicum. II. E. K. NELSON (*J. Amer. Chem. Soc.*, 1920, **42**, 597—599. Compare A., 1919, i, 543).—Octovanillylamide (this vol., i, 154), like capsaicin, is very stable towards alkalis, and is somewhat soluble in concentrated hydrochloric acid; also, free ammonia is easily liberated from free vanillylamine when it is boiled with water or solutions of alkaline carbonates, thus explaining its observation by Lapworth and Royle during the alkaline reduction of capsaicin (T., 1919, **115**, 1109). The objections of these workers to the formulation of capsaicin as decenovanillylamide thus lose their force, and the author has now confirmed this formula by the regeneration of capsaicin from decenoyl chloride (obtained from the decenoic acid produced from capsaicin) and vanillylamine.

Indefinite results have been obtained from the oxidation of decenoic acid by chromic acid. By fusion with potassium hydroxide, acetic acid and an octoic acid, b. p. 240—245°, with a branched carbon chain, are produced. The *silver octoate*, $C_8H_{15}O_2Ag$, is sparingly soluble in water. J. K.

Influence of the Sulphonation of the Phenol on the Yields of Picric Acid. M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], **27**, 195—199).—The yield of picric acid depends on the relative proportions of phenolsulphonic acid and phenoldisulphonic acid in the products of sulphonation of the phenol, the yields being much higher from the disulphonic acid. The maximum yield of phenoldisulphonic acid is obtained by carrying out the sulphonation for half an hour to one hour at 100° with five parts of 93% sulphuric acid to one part of phenol. W. G.

The Identification of Phenols. II. JAMES A. LYMAN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1920, **42**, 615—619. Compare A., 1917, i, 333).—*p*-Nitrobenzyl ethers have been prepared from a number of phenols. It is advisable to employ as solvents for the etherification of esters of salicylic acid the respective alcohols from which they are derived, and to avoid excess of alkali; otherwise interchange of the alkyl groups of the alcohol and of the ester takes place to a certain extent (compare Pardee and Reid, *J. Ind. Eng. Chem.*, 1920, **12**, 129). The p-*nitrobenzyl ethers* of the following phenols had the melting points indicated: *o*-nitrophenol, 130°; *p*-nitrophenol, 187·4°; 2:4-dinitrophenol, 248°; *o*-chlorophenol, 100°; *p*-chlorophenol, 101·3°; 2:4:6-tribromophenol, 163·5°; guaiacol, 63·6°; *a*-naphthol, 140°; *β*-naphthol, 106·5°; salol, 87°; methyl salicylate, 128·2°; ethyl salicylate, 125°; butyl salicylate, 92°; *o*-tolyl salicylate, 142·5°; *m*-tolyl salicylate, 118°. J. K.

A Comparison of the Activity of certain Unsaturated Groups with the Activity of the Allyl Group in certain Ethers. S. G. POWELL and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 646—658).—A comparison of various unsaturated ethers with phenyl allyl ethers in respect of the rearrangement of the latter into *o*-allylphenols. Of compounds containing, like the allyl derivatives, an unsaturated linking in the *βγ*-position to the oxygen atom, phenyl and *p*-bromophenyl propargyl ethers do not yield phenolic compounds when boiled, but suffer complete decomposition; phenoxyacetonitrile was decomposed to some extent when boiled, whilst a tarry product resulted from its *p*-methyl derivative, which, however, gave a little *p*-cresol when its solution in amyl ether was boiled; the chief products of decomposition of the benzyl ethers were not diphenylmethane, but benzene, derivatives, and their *p*-nitro- and *p*-bromo-derivatives suffered more or less profound decomposition. Contrary to the statement of D.R.-P. 268099, phenyl and *p*-tolyl vinyl ethers do not suffer rearrangement, but decompose when heated, yielding phenol and *p*-cresol. *δ*-Phenoxy-Δ^{α}-butene, *ε*-phenoxy-Δ^{β}-pentene, and its *β*-methyl derivatives were all remarkably stable, and suffered neither rearrangement nor decomposition when boiled.

Phenyl vinyl ether, CH_2:CH·OPh, from phenyl *β*-bromoethyl ether, b. p. 155—156°; p-*tolyl vinyl ether*, C_6H_4Me·O·CH:CH_2, similarly prepared, with a pleasant odour, has b. p. 177—180°; n_D^{20} 1·513; D_{25}^{20} 0·975; *β*-p-*bromophenoxyethyltrimethylammonium bromide*, C_6H_4Br·O·CH_2·CH_2·NMe_3Br, white crystals, from *p*-bromophenyl *β*-bromoethyl ether and trimethylamine. *γ-Phenoxypropylmethylcarbinol*, OPh·[CH_2]$_3$·CHMe·OH, prepared by reduction of *γ*-phenoxypropyl methyl ketone, is a viscous oil, having b. p. 163°/20 mm., n_D^{25} 1·5123, D_{25}^{21} 1·025; by treatment with phosphorus tribromide; *β-bromo-ε-phenoxypentane*, OPh·[CH_2]$_3$·CHMeBr, is obtained. It is an oil, b. p. 172°/28 mm., with n_D^{20} 1·529, D_{25}^{20} 1·258, and with alcoholic potash gives *ε*-phenoxy-Δ^{β}-pentene. *ε-Phenoxy-β-methyl-*Δ^{β}*-pentene*,

OPh·[CH_2]$_2$·CH:CMe_2,

b. p. 241°/745 mm., n_D^{20} 1·505, is prepared by fractionation of the product of the action of magnesium methyl iodide on ethyl γ-phenoxybutyrate. *Phenyl β-bromoallyl ether*, $OPh\cdot CH_2\cdot CBr\vdots CH_2$, for the preparation of phenyl propargyl ether, is best obtained from sodium phenoxide and tribromohydrin. Similarly, p-*bromophenyl β-bromoallyl ether*, $C_6H_4Br\cdot OCH_2\cdot CBr\vdots CH_2$, is prepared from sodium *p*-bromo phenoxide as an oil, b. p. 171°/22 mm., n_D^{22} 1·587, D_{25}^{25} 1·719; p-*bromophenyl propargyl ether*, $C_6H_4Br\cdot O\cdot CH_2\cdot C\vdots CH$, has b. p. 144°/24 mm., n_D^{20} 1·567, and D_{25}^{25} 1·468; p-*bromophenoxyacetamide*,

$$C_6H_4Br\cdot O\cdot CH_2\cdot CO\cdot NH_2,$$

forms needles, m. p. 148—149°; p-*methoxyphenyl* p-*nitrobenzyl ether*, $C_{14}H_{13}O_4N$, forms yellow needles, m. p. 88°; p-*bromophenyl* p-*nitrobenzyl ether*, $C_{13}H_{10}O_3NBr$, yellow needles, m. p. 112°; 2 : 4-*dibromophenyl* p-*nitrobenzyl ether*, $C_{13}H_9O_3NBr_2$, yellow needles, m. p. 161°.

J. K.

Preparation of Derivatives of *N*-Acylated-*p*-aminophenols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 316902; from *Chem. Zentr.*, 1920, ii, 374).—*N*-Acyl derivatives of *p*-aminophenols are caused to react with α-bromo-α-ethylbutyrylcarbimide. Thus, the *α-bromo-α-ethylbutyrylurethane* of p-*acetylaminophenol*, $CEt_2Br\cdot CO\cdot NH\cdot CO_2\cdot C_6H_4\cdot NHAc$ (from bromoethylbutyrylcarbimide and a suspension of *p*-acetylaminophenol in acetone), forms small, colourless, shining leaflets, m. p. 144°. The *α-bromo-α-ethylbutyrylcarbamic ester* of p-*hydroxyphenylcarbamide*, colourless crystals, has m. p. 187°. The products exhibit marked antipyretic and antineuralgic, and distinct sedative and hypnotic, action.

H. W.

Phenoltrisulphonic Acid and its Transformation into Picric Acid. M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], **27**, 199—204).—By the sulphonation of phenol with ten times its weight of sulphuric acid containing 20% of sulphur trioxide, a mixture of phenol-di- and -tri-sulphonic cids is obtained, which contains 80% of the trisulphonic acid. On nitration, the trisulphonic acid gives a yield of picric acid equivalent to 90% of theory. Thus, in the nitration of the phenolsulphonic acids, the yield of picric acid increases from the mono- up to the tri-sulphonic acid. The ionisation of these acids increases in the same order. Phenoltrisulphonic acid gives two *barium* salts,

$$[OH\cdot C_6H_2(SO_3)_3]_2Ba_3,2H_2O$$

and $C_6H_2\overset{\text{---}O\text{---}}{\lessgtr_{(SO_3)_3}}\!\!\geqslant Ba_2$, and a *sodium* salt,

$$OH\cdot C_6H_2(SO_3Na)_3,3H_2O.$$

The barium salt is only very sparingly soluble in water, but barium sulphate may be washed free from it by 5% hydrochloric acid.

W. G.

The Hydrolysis of Naphthyl Ethers. GOPAL BALKRISHN KOLHATKAR (*J. Ind. Inst. Sci.*, 1919, **2**, 179—186).—β-Naphthyl

ethers are much more readily hydrolysed by hydrochloric acid than the corresponding α-naphthyl ethers, whilst the corresponding phenyl ethers are only decomposed to a very slight extent under similar conditions. β-Naphthyl methyl ether is more readily hydrolysed than β-naphthyl ethyl ether. The amount of ether hydrolysed is practically independent of the amount of ether present, but is approximately proportional to the volume of acid present, and the time of the reaction, and is also influenced by the concentration of the acid. W. G.

Preparation of Tetrahydro-β-naphthyl Mercaptan. GEORG SCHROETER and WALTHER SCHRAUTH (D.R.-P. 299604; from *Chem. Zentr.*, 1920, ii, 447).—Tetrahydronaphthalene is converted by chlorosulphonic acid into tetrahydronaphthalene-β-sulphonyl chloride, which is then treated with reducing agents. The *sulphonyl chloride* has m. p. 55—56°, b. p. 194—195°/14 mm., and is converted by ammonia into *tetrahydronaphthalene-β-sulphonamide*, m. p. 134—135°, and by potassium hydroxide solution (50%) into the crystalline potassium tetrahydronaphthalene-β-sulphonate. The sulphonyl chloride is reduced by zinc dust and sulphuric or hydrochloric acid to *tetrahydro-β-naphthylmercaptan*, b. p. 153—155°/26 mm., which has only a faint odour of mercaptan and yields a colourless, well-crystallised mercury salt. It is converted by methyl sulphate and alkali into the corresponding *methyl ether*, colourless, aromatic oil, b. p. 151°/14 mm. *Tetrahydronaphthylthiolacetic acid*, $C_{10}H_{11}\cdot S\cdot CH_2\cdot CO_2H$, m. p. 133—135°, is formed by the action of chloroacetic acid on a solution of the thiol in sodium hydroxide, and subsequent addition of acid. An ammoniacal solution of the mercaptan is oxidised by air to *bistetrahydronaphthyl disulphide*, $(C_{10}H_{11})_2S_2$, m. p. 87—89°. The "thionaphthol" is designed for the preparation of drugs, disinfectants, dyes, and explosives. H. W.

1:2:2:3-Tetramethyl*cyclo*pentane-1-carbinol and its Derivatives. H. RUPE and P. LÄUGER (*Helv. Chim. Acta*, 1920, **3**, 272—298).—The purposes of experimental stereochemistry demand a primary alcohol, of considerable optical activity, and easily convertible into stable esters, including those of the halogen acids. Myrtenol fulfils these requirements (A., 1915, ii, 717; Zäslin, *Diss.*, Basel, 1915), but is not easily accessible. Camphylcarbinol, otherwise suitable, is too readily dehydrated (A., 1919, i, 29). The authors have therefore studied anew the reduction of the carboxyl group of campholic acid by the method of Bouveault and Blanc, these workers having obtained very small yields in this case (A., 1904, i, 642). Apparently the first stage of such reductions consists in the addition of hydrogen with the formation of a hydro-derivative, because the yields in the present case gradually increase with the degree of unsaturation of the residue of the hydroxy-compound from which the ester is derived. Thus the ethyl, the *iso*butyl, the *iso*amyl, the β-naphthyl, and the phenyl esters respectively give yields of 10—15%, 22%, 25%, 64%, and 94—96%.

β-Naphthyl campholate, $C_9H_{17}\cdot CO\cdot O\cdot C_{10}H_7$, silky leaflets, m. p. 70°, is obtained from campholic chloride and either β-naphthol or its sodium salt. Phenyl campholate, prepared in a similar way, is a liquid, b. p. 163°/10 mm. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentane*-1-*carbinol*, $C_9H_{17}\cdot CH_2\cdot OH$, prepared by reduction of phenyl campholate under carefully regulated conditions, for which the original should be consulted, is a waxy mass, m. p. 64°, b. p. 96—96·5°/10 mm., with a disagreeably penetrating odour, reminiscent of that of fenchyl alcohol; in benzene, it has $[\alpha]_C^{20}$ +53·36°; $[\alpha]_D^{20}$ +67·18° $[\alpha]_{Hg(\lambda=546\cdot3)}^{20}$ +79·42°; $[\alpha]_F^{20}$ +102·74°. The *benzoate*,

$$C_9H_{17}\cdot CH_2\cdot O\cdot CO\cdot C_6H_5,$$

is a viscid, colourless oil, almost odourless, b. p. 186°/12 mm. The corresponding aldehyde may be obtained from the alcohol by direct oxidation, or by Bouveault's catalytic process with copper, but the yields are poor. Better results are obtained by Merling's process (*A.*, 1908, i, 653), which involves the following series of reactions. Campholic chloride is converted into the *anilide*, $C_9H_{17}\cdot CO\cdot NHPh$, leaflets, m. p. 93°. The crude phenyliminochloride, obtained by treatment of the anilide with phosphorus pentachloride, reacts vigorously with aniline, with the production of the *diphenylamidine*, $C_9H_{17}\cdot C(:NPh)\cdot NHPh$, leaflets, m. p. 211°; this compound, by reduction in alcoholic solution with sodium, furnishes 1 : 2 : 2 : 3-*tetramethyl*cyclo*pentane*-1-*diphenylmethylenediamine*,

$$C_9H_{17}\cdot CH(NHPh)_2,$$

leaflets, m. p. 76—77°. This product, in its crude condition, after removal of impurities volatile in steam, is hydrolysed by the addition of sulphuric acid and continuing the steam distillation. The yield is 45—55%. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentane*-1-*aldehyde*, $C_9H_{17}\cdot CHO$, m. p. 37—38°, b. p. 73—74°/8 mm., resembles camphor in appearance, and has a somewhat disagreeable and penetrating odour. It has a burning taste. In alcoholic solution it slowly reduces Fehling's solution. In benzene, $[\alpha]_C^{20}$ +68·48°; $[\alpha]_D^{20}$ +89·26°; $[\alpha]_{Hg}^{20}$ +108·00°; $[\alpha]_F^{20}$ +148·65°. It is characterised by its *semicarbazone*, fine needles, m. p. 220—221° (decomp.), its *oxime*, m. p. 27—28°, b. p. 116·5—117°/8 mm., its *phenylhydrazone*, a yellow oil, b. p. 189—190°/8 mm., easily decomposed even at ordinary temperatures; its p-*nitrophenylhydrazone*, yellow leaflets, m. p. 145°; and its p-*bromophenylhydrazone*, red leaflets, m. p. 145—146°. *Ethyl* β-*hydroxy*-1 : 2 : 2 : 3-*tetramethyl*cyclo*pentane*-1-*propionate* $C_9H_{17}\cdot CH(OH)\cdot CH_2\cdot CO_2Et$, from the aldehyde, ethyl bromoacetate and zinc, is a yellow oil, b. p. 151—152°/10 mm. or 264°/730 mm.; its *acetyl* derivative, $C_9H_{17}\cdot CH(O\cdot Ac)\cdot CH_2\cdot CO_2Et$, is a colourless, viscid oil, b. p. 165—167°/13 mm. β-*Hydroxy*-1 : 2 : 2 : 3-*tetramethyl*cyclo*pentane*-1-*propionic acid*, $C_9H_{17}\cdot CH(OH)\cdot CH_2\cdot CO_2H$, prepared from the ester by hydrolysis with alcoholic potash, forms leaflets, m. p. 79·5—80° (decomp. 140°), but can be distilled almost without decomposition at 191—193°/10 mm. By dehydration with acetic anhydride it furnishes 1 : 2 : 2 : 3-*tetramethyl*cyclo*pentane* - 1 - *acrylic acid*, $C_9H_{17}\cdot CH:CH\cdot CO_2H$, long needles, m. p. 101°; this compound may also be obtained by hydro-

lysis of the above acetyl derivative, or by distilling under reduced pressure *ethyl β-bromo*-1 : 2 : 2 : 3-*tetramethyl*cyclo*pentane*-1-*propionate*, C_9H_{17}·CHBr·CH_2·CO_2Et, a yellow oil, produced by the action of phosphorus tribromide on the hydroxy-ester. The acrylic acid is sparingly soluble in water, but readily in organic solvents; in benzene, $[\alpha]_C^{20}$ + 52·06°; $[\alpha]_D^{20}$ + 66·82°; $[\alpha]_{Hg}^{20}$ + 79·90°; $[\alpha]_F^{20}$ + 107·39°. The *methyl* ester, $C_{13}H_{22}O_2$, is an oil, b. p. 131—132°/12 mm.; the *chloride*, $C_{12}H_{19}OCl$, an oil, b. p. 139°/13 mm.; the *ethyl* ester, $C_{14}H_{24}O_2$, an oil, b. p. 149°/12 mm., has $[\alpha]_C^{20}$ + 44·91°; $[\alpha]_D^{20}$ + 57·51°, $[\alpha]_{Hg}^{20}$ + 68·80°, $[\alpha]_F^{20}$ + 91·93°, and in benzene the values are + 44·47°, 57·11°, 68·19°, and 91·50°. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentane*-1-*propionic acid*, C_9H_{17}·CH_2·CH_2·CO_2H, is prepared by reduction of the acrylic acid in aqueous alcoholic solution in presence of a 40% nickel catalyst (A., 1919, i, 29); it crystallises in large, thin leaflets, m. p. 89·5—90°, and in benzene has $[\alpha]_C^{20}$ + 36·21°, $[\alpha]_D^{20}$ + 48·38°, $[\alpha]_{Hg}^{20}$ + 57·20°, $[\alpha]_F^{20}$ + 75·29°; the *magnesium salt*, $[C_{12}H_{21}O_2]_2Mg$, *forms leaflets; the chloride*, $C_{12}H_{21}OCl$, is an oil, b. p. 129°/12 mm.; the *ethyl* ester, $C_{14}H_{26}O_2$, boils at 138°/12 mm. and has $[\alpha]_C^{20}$ + 32·32°; $[\alpha]_D^{20}$ + 40·95°; $[\alpha]_{Hg}^{20}$ + 48·59°; $[\alpha]_F^{20}$ + 63·15°, whilst in benzene the values are + 32·94°, 41·66°, 49·14°, and 64·54°. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentylmethylcarbinol*, C_9H_{17}·CHMe·OH, from the above aldehyde and magnesium methyl iodide, is a clear liquid, b. p. 96—98°/11 mm., with a faint odour of camphor; on oxidation it yields 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl methyl ketone, b. p. 96—102°/12 mm. (Rupe and Kloppenburg, A., 1919, i, 539; Meerwein, A., 1919, i, 162). *Phenyl* 1 : 2 : 2 : 3-*tetramethyl*cyclo*pentylcarbinol*, C_9H_{17}·CHPh·OH, m. p. 55°, b. p. 172—174°/11 mm., could not be oxidised to the ketone. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentylstyrene*, C_9H_{17}·CH:CHPh, is obtained by boiling the crude condensation product from magnesium benzyl chloride and the above aldehyde with acetic anhydride, and forms leaflets with a blue fluorescence, m. p. 51°, b. p. 146—149°/11 mm. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentylbenzylcarbinyl acetate*,

$$C_9H_{17}\cdot CH(OAc)\cdot CH_2\cdot C_6H_5,$$

needles, m. p. 81—82°, b. p. 189—192°/11 mm., is also produced in the reaction. J. K.

Arbusterol and its Derivatives. GIOVANNI SANI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 59—61).—*Arbusterol*,

$$C_{26}H_{43}\cdot OH,H_2O,$$

isolated from the oil of *Arbutus unedo* seeds, crystallises in aggregates of silky, white needles, resembling bits of straw, m. p. 129°, $[\alpha]_D^{18}$ − 15·33°, its specific rotation being thus widely different from those of other phytosterols. In chloroform solution it gives with sulphuric acid a cherry-red coloration, changing to dirty violet with a purple reflexion, whilst the acid becomes at first yellow and later brown, with a green fluorescence. Its *benzoyl* derivative, $C_{26}H_{43}$·OBz, forms shining, elongated, rectangular scales, m. p. 137°, and its *acetyl* derivative, $C_{26}H_{43}$·OAc, crystals, m. p. 110°. The pro-

portions of halogens fixed by arbusterol differ from those fixed by other cholesterols, and are being further investigated. T. H. P.

Volatility in Steam: Benzoic Acid and its Derivatives. NEVIL VINCENT SIDGWICK (T., 1920, **117**, 396—406).

The Use of Oxalyl Chloride and Bromide for Producing Acid Chlorides, Acid Bromides, or Acid Anhydrides. III ROGER ADAMS and L. H. ULICH (*J. Amer. Chem. Soc.*, 1920, **42** 599—611).—When the method of preparation of aromatic anhydride from 1 mol. of oxalyl chloride and 2 mols. of acid (A., 1918, i, 165 is applied to *m*- or *p*-nitro-, 3:5-dinitro-, or 2:4:6-trinitro-benzoi acid, mixed anhydrides, very stable towards excess of chloride, ar obtained, and these, except in the case of the last compound, whe melted give the simple anhydrides. Probably, therefore, in genera the course of the reaction is expressed as follows: $2RCO_2H + (COCl)_2 \longrightarrow 2HCl + (R{\cdot}CO_2{\cdot}CO)_2 \longrightarrow (R{\cdot}CO)_2O + CO_2$. Less favour able results are obtained with aliphatic acids than with aromati compounds, some acid beiug unchanged, and some acid chlorid being produced. Acid chlorides may be prepared smoothly and i good yield by boiling acid anhydrides, including those of the nitr compounds above, with 1·5—2·5 mols. of oxalyl chloride alone or i presence of benzene for two hours; the anhydrides may he replace by aromatic or aliphatic acids themselves, but in this case tl nitrobenzoic acids only give the mixed anhydrides. Arsenic tr chloride and chromyl chloride were also successfully prepared fro their oxides by this method. Either anbydrides or chlorides ar however, better prepared from the sodium salts of the acids an 1 or 1—1·5 mols. respectively of oxalyl chloride in benzene solutio Possibly, in this case, mixed anhydrides are not intermediate pr ducts, because the nitrobenzoic acids do not exhibit the exception behaviour previously noted. Oxalyl bromide behaves in a simil manner to the chloride; better yields of acid bromides we obtained than with phosphorus pentabromide.

Excellent yields of benzanilide, anisanilide, and *p*-toluanilic were obtained from ethereal solutions of the appropriate ketoxim on adding 0·75 mol. oxalyl chloride, which therefore promotes tl Beckmann rearrangement very effectively.

p-*Nitrobenzoic oxalic anhydride*, $C_2O_2(O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2)_2$, yello crystals, which melt and decompose at 169—170°.

2:4:6-*Trinitrobenzoic oxalic anhydride*,

$$C_2O_2[O{\cdot}CO{\cdot}C_6H_2(NO_2)_3]_2,$$

yellow crystals, melts and decomposes at 228—230°, but, unlike tl other anhydrides of this type, furnishes 1:3:5-trinitrobenzene, ar with sodium carbonate solution easily gives sodium trinitrobenzoat

o-*Chlorobenzoyl bromide*, $C_6H_4Cl{\cdot}COBr$, has b. p. 143—145° 37 mm.; m-*chlorobenzoyl bromide*, b. p. 143—147°/40 mm p-*chlorobenzoyl bromide*, b. p. 141—143°/27 mm.; *o*-bromobenzo bromide, b. p. 166—168°/18 mm.; p-*bromobenzoyl bromide*, b. 135—137°/18 mm.; p-*iodobenzoyl bromide*, m. p. 54—55°, rapid

darkens; o-*toluoyl bromide*, b. p. 133—136°/37 mm.; m-*toluoyl bromide*, b. p. 136—137°/52 mm.; p-*toluoyl bromide*, b. p. 145—149°/42 mm.; p-*methoxybenzoyl bromide*, b. p. 183—186°/27 mm.; m-*nitrobenzoyl bromide*, m. p. 42—43°, b. p. 165—167°/18 mm.; p-*nitrobenzoyl bromide*, m. p. 63—64°; 3:5-*dinitrobenzoyl bromide*, m. p. 59—60°; *cinnamyl bromide*, m. p. 47—48°, b. p. 180—184°/40 mm.; *phenylacetyl bromide*, b. p. 150—155°/50 mm.

J. K.

Alcoholysis. III. The Alcoholysis of Aromatic Esters and the Inhibiting Influence of Ortho-substituents. J. J. SUDBOROUGH and D. D. KARVÉ (*J. Ind. Inst. Sci.*, 1919, **3**, 1—14. Compare this vol., i, 364).—The results obtained with a large number of esters of aromatic acids indicate quite clearly that sodium alkyloxides or hydrochloric acid are excellent catalysts for the alcoholysis of these esters. An ethyl ester may readily be converted into the corresponding methyl ester by dissolving it in ten times its weight of methyl alcohol, adding a small piece of sodium, and warming for ten minutes. Two substituents in ortho-positions to the ester group completely inhibit the change. The following new esters have been prepared and characterised.

Ethyl 3:5-*dibromobenzoate*, m. p. 51°, is obtained by eliminating the amino-group from *ethyl* 3:5-*dibromo*-4-*aminobenzoate*, m. p. 108°, which is prepared by brominating ethyl *p*-aminobenzoate in dilute sulphuric acid solution. *Methyl* 3:5-*dibromo*-4-*aminobenzoate* has m. p. 127—128°; *ethyl* 2:4:6-*tribromobenzoate*, m. p. 80°. *Ethyl* 2:4:6-*tribromo*-3-*aminobenzoate*, m. p. 61—62°, was prepared from the silver salt of the acid and ethyl iodide. *Methyl* 2:4:6-*tribromo*-3-*aminobenzoate* has m. p. 96—97°. *Ethyl* 2:3:4:6-*tetrabromobenzoate* has m. p. 31°; iso*butyl* p-*nitrobenzoate* has m. p. 64—65°; *propyl* 3:5-*dinitrobenzoate* has m. p. 71°; iso*butyl* 3:5-*dinitrobenzoate* has m. p. 85°; *ethyl* 2:6-*dinitrobenzoate* has m. p. 75·5°.

W. G.

Preparation of p-Carbamidophenylacetylcarbamide and Related Compounds. MARY RISING (*J. Amer. Chem. Soc.*, 1920, **42**, 128—136. Compare Rising and Stieglitz, A., 1918, i, 271).—The successful preparation of *p*-carbamidophenylacetylcarbamide is described as the first of a series of carbamidophenylacylcarbamides which are intended to form a basis for the study of their physiological activity, particularly as hypnotics.

p-Nitrophenylacetyl chloride is condensed with carbamide in boiling benzene to yield *p*-nitrophenylacetylcarbamide, m. p. 237—239°, after preliminary softening and depending on the rate of heating (Jacobs and Heidelberger, A., 1918, i, 90, give m. p. 250—252°). This substance is quantitatively reduced by a solution of stannous chloride in cold glacial acetic acid which has been saturated with hydrogen chloride to p-*aminophenylacetylcarbamide*, which decomposes without melting at 192—193°, and, in the form of its *hydrochloride*, is converted by potassium cyanate into p-*carbamidophenylacetylcarbamide*, $NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot NH_2$.

The preparation of the following related carbamide derivatives is also described: methyl *p*-aminophenylacetate, b. p. 140—150°/17 mm., and its hydrochloride from *p*-aminophenylacetonitrile; p-*carbamidophenylacetonitrile*, m. p. 170·5°, from potassium cyanate and *p*-aminophenylacetonitrile hydrochloride; *methyl* p-*carbamidophenylacetate*, colourless, shining needles, m. p. 131—132°, by the esterification of *p*-carbamidophenylacetonitrile and from methyl *p*-aminophenylacetate hydrochloride and potassium cyanate; *p*-carbamidophenylacetic acid, m. p. 184—185° (decomp.), by hydrolysis of the corresponding methyl ester.

The ethylation of phenylacetonitrile with metallic sodium or sodamide and ethyl iodide is fully discussed. H. W.

α-Bromo-*o*- and -*p*-nitrocinnamic Acids. S. REICH and N. Y. CHANG (*Helv. Chim. Acta*, 1920, **3**, 235—240).—A mixture of the two stereoisomeric ethyl α-bromo-*p*-nitrocinnamates is produced in quantitative yield when an alcoholic solution of equimolecular proportions of ethyl αβ-dibromo-β-*p*-nitrophenylpropionate and anhydrous sodium acetate is boiled for two hours. The esters may be separated mechanically after crystallisation from light petroleum, and undergo hydrolysis to the respective acids by treatment at 100° with a mixture of glacial acetic acid (five parts), sulphuric acid (one part), and water (one part). *allo*-α-Bromo-*p*-nitrocinnamic acid, like its meta-isomeride (Reich and others, A., 1918, i, 262), does not undergo condensation into a dibromodinitrotruxone when treated with sulphuric acid; it is unchanged by the cold acid, whilst at 100° it is converted into its stable isomeride. *Ethyl* allo-*α-bromo-o-nitrocinnamate*,

$$NO_2\cdot C_6H_4\cdot CH\colon CBr\cdot CO_2Et,$$

is a yellow oil, which does not solidify, and results as the sole product of the action of sodium acetate on ethyl αβ-dibromo-β-*o*-nitrophenylpropionate. By hydrolysis under the above conditions, it is converted into the stable form of the corresponding acid (Naar, A., 1882, 840), the stability of the *allo*-forms of the three *allo*-α-bromonitrocinnamic acids and their esters increasing in the order ortho-, meta-, para-. αβ-Dibromo-β-*p*-nitrophenylpropionic acid furnishes a *bromo*-p-*nitrostyrene*, $NO_2\cdot C_6H_4\cdot CH\colon CHBr$, pale yellow needles, m. p. 45—46°, by treatment with sodium acetate in absolute alcoholic solution; if aqueous sodium acetate or sodium carbonate be used, a *stereoisomeride*, pale yellow needles, m. p. 123°, is obtained. The same tribromo-compound, m. p. 83°, is produced from each by the action of bromine. *Bromo-o-nitrostyrene*, $NO_2\cdot C_6H_4\cdot CH\colon CHBr$, is similarly obtained in two forms, yellow, m. p. 70°, and a yellow oil, which each furnish a tribromo-compound, m. p. 80°. J. K.

Influence of the Weight of Radicles on the Isomerisation of Ethylenic Compounds. S. REICH and RENÉE COUCHET (*Helv. Chim. Acta*, 1920, **3**, 240—243).—allo-*α-Bromocinnamtribromo-*

nilide, $C_{15}H_9ONBr_4$, m. p. 193°, accompanied by a small quantity f the *diallo-α-bromocinnamyl derivative*,

$$[CHPh\colon CBr\cdot CO]_2\colon N\cdot C_6H_2Br_3,$$

ı. p. 150°, was prepared from the acid by treatment successively rith phosphorus pentachloride in ethereal solution and tribromoniline in benzene solution. By exposure in benzene solution to ght for sixty hours, or in presence of bromine in chloroform olution, it is changed into the stable *isomeride*, needles, m. p. 50°. This compound was also prepared in a similar manner from s acid, the treatment with phosphorus pentachloride being carried ut in boiling toluene solution. *allo*-α-Bromocinnamic anhydride Michael and Bucher, A., 1898, i, 256) is produced by the action f acetic anhydride on the acid. It is isomerised by exposure to ght for two weeks, but not by bromine. The latter result is ossibly due to failure of the bromine to attach itself to the double ond rather than to the weight of the radicle. Stable *α-bromonnamic anhydride*, $C_{18}H_{18}O_3Br_2$, prepared in a similar manner, rms needles, m. p. 100°. J. K.

The Truxillic Acids. A. W. K. de Jong (*Proc. K. Akad. etensch. Amsterdam*, 1920, **22**, 509—511).—The truxillic acids ay best be separated from cinnamic acid by sublimation in a ırrent of air at 130°. The truxillic acids may be separated from ıe another by the following process. The mixture of acids is ssolved in the calculated quantity of *N*/10-potassium hydroxide, ıd to the solution 1·5 grams of anhydrous calcium chloride are lded for each 10 c.c. After twenty-four hours, the precipitated lcium salts of β-, δ-, and ε-truxillic acids are filtered off. The her acids are separated from the filtrate by hydrochloric acid ıd ether, and the process as above is repeated. To the final trate 8·5 grams of calcium chloride are added for each 10 c.c., e calcium salt of β-cocaic acid being precipitated and filtered f. From the filtrate, α- and γ-truxillic acids are separated by ydrochloric acid and ether, and the γ-acid is finally separated from e α-acid by its solubility in hot water. The mixture of calcium lts of β-, δ-, and ε-truxillic acids, obtained as above, is conrted into the barium salts, which are separated by their varying lubility in water.

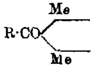
β-Cocaic acid gives with cinnamic acid a crystalline double acid, . p. 139°. The ammonium salts of the truxillic acids slowly lose eir ammonia when their aqueous solutions are evaporated on a ıter-bath, and are transformed into the free acids. W. G.

Action of Cyanogen Bromide on Hydrocarbons and henol Ethers under the Influence of Aluminium Chloride. Karrer, A. Rebmann, and E. Zeiler (*Helv. Chim. Acta*, 1920, 261—272).—A study of the range of applicability of the process the synthesis of nitriles recently described (A., 1919, i, 591). ccellent yields were obtained of 3-cyanoacenaphthene and cyanothiophen (owing to the agreement in properties between

line *compounds*, $C_{22}H_{24}O_2$, one having m. p. 117—118°, and the other m. p. 188—190°, which are apparently products of the abnormal condensation of one molecule of dimethyl*cyclo*hexanone with two molecules of benzaldehyde. The authors agree with Auwers and Krollpfeiffer (*loc. cit.*) that the dimethyl*cyclo*hexanone under examination is a 1 : 1-*dimethyl-2-compound*.

W. G.

Condensation of Acetophenone by means of Sodium Ethoxide. II. C. Castaldi (*Gazzetta*, 1920, **50**, i, 71—81. Compare A., 1916, i, 31).—The author has investigated further the compound, m. p. 182°, obtained as one of the products of the condensation of acetophenone with sodium ethoxide (*loc. cit.*). This compound is probably identical with the one, m. p. 183°, obtained by Stobbe (A., 1901, i, 549) by condensing acetophenone with ethyl malonate by means of dry sodium ethoxide in presence of anhydrous ether; this author attributed to it the formula $C_{24}H_{18}O$, and, on the basis of its failure to react with phenylhydrazine or hydroxylamine, considered that the oxygen atom is not present as carbonyl. By the work of Feith and Davies (A., 1892, 314), Hantzsch (A., 1891, 35), and Baum (A., 1896, i, 222), it has, however, been shown that the carboxylic oxygen of the group (annexed formula) reacts with phenylhydrazine or hydroxylamine only when R is a carboxyl group, and not when it is either methoxyl or phenyl.



Gentle oxidation of the compound with nitric acid yields either 6-benzoyl-3 : 5-diphenylbenzoic acid or 4-benzoyl-3 : 5-diphenylbenzoic acid, the sodium salt of which yields 1 : 3-diphenylbenzene, carbon dioxide, and benzene (?) when dry-distilled. The compound must, therefore, be regarded as either 6-benzoyl-3 : 5-diphenyltoluene or 4-benzoyl-3 : 5-diphenyltoluene, and confirmation of this structure is afforded by the fact that it is obtainable also by the action of benzoyl chloride on 3 : 5-diphenyltoluene in carbon disulphide solution and in presence of aluminium chloride.

6-*Benzoyl*-3 : 5-*diphenyltoluene* or 4-*benzoyl*-3 : 5-*diphenyltoluene*, $C_{26}H_{20}O$, forms shining laminæ, m. p. 186° (not 182° as previously stated), has the normal molecular weight in freezing benzene, and dissolves in cold concentrated sulphuric acid, giving an intense violet-red solution.

6-*Benzoyl*-3 : 5-*diphenylbenzoic acid* or 4-*benzoyl*-3 : 5-*diphenylbenzoic acid*, $C_{26}H_{18}O_3$, forms faintly yellow, prismatic needles, m. p. 240° (decomp.), and dissolves in the cold in concentrated sulphuric acid, giving an intense violet coloration. The *sodium* salt (+ $4H_2O$) was prepared.

Diphenylbenzyltoluene, $C_6H_2MePh_2{\cdot}CH_2Ph$, obtained by reducing the benzoyldiphenyltoluene by means of red phosphorus and hydriodic acid, crystallises in colourless needles, m. p. 125°, and gives no coloration with concentrated sulphuric acid.

T. H. P.

Reduction and Fission of Halogenated Ketones by Tertiary Bases. KARL VON AUWERS and ELISABETH LÄMMERHIRT (*Ber.*, 1920, **53**, [*B*], 428—443).—The conversion of *m*-*a*-bromo*iso*butyryl-*p*-cresol into 3:6-dimethylchromanone by the action of boiling dimethyl- or diethyl-aniline (A., 1914, i, 1136) does not appear to be an instance of a general reaction, since the examination of a series of *a*-halogenated acyl-*p*-cresols shows that, as a rule, the parent halogen-free compound is regenerated, whilst chromanones or coumaranones are only formed in relatively small amount. The detection of coumaranones in the presence of keto-phenols is best effected with the aid of *p*-nitrophenylhydrazine, which converts the former into the sparingly soluble dinitro-osazones of the corresponding diketones, and the latter into the more readily soluble nitrophenylhydrazones. The same reagent may be used to distinguish between coumaranones and chromanones, since the latter, like the monocyclic ketones, only yield readily soluble mono-derivatives. The separation of keto-phenols and chromanones is not smoothly effected by treatment with alkali hydroxides, and is best accomplished by protracted warming of the mixture with semicarbazide. Mixtures of free keto-phenols and their ethers, such as are frequently obtained by the condensation of phenol ethers with acid chlorides in the Friedel-Craft's reaction, are not readily separated by means of alkali hydroxide and ether; removal of the phenols is, however, effected by shaking the solution of the mixed substances in light petroleum with aqueous methyl-alcoholic potassium hydroxide solution (compare Claisen, A., 1919, i, 266).

o-Chloroacetyl-*p*-cresol, when boiled with diethylaniline, is mainly converted into 4-methylcoumaranone (*identified as the dinitro-osazone* of p-*tolylglyoxal*, m. p. 260—265° [subsequent communication]), small amounts of acetyl-*p*-cresol (p-*nitrophenylhydrazone*, orange-red, shining needles, m. p. 245—246°) being also formed. Under similar conditions, *o*-*a*-chloropropionyl-*p*-cresol gives *o*-propionyl-*p*-cresol (p-*nitrophenylhydrazone*, m. p. 185—186°) and a little 1:4-dimethylcoumaranone. *o*-*a*-Bromo-*n*-butyryl-*p*-cresol yields o-*butyryl*-p-*cresol*, coarse, shining prisms, m. p. 33—34° (*semicarbazone*, long needles, m. p. 188—189°), and 2:6-dimethylchromanone. *o*-*a*-Chloro*iso*valeryl-*p*-cresol is smoothly reduced by dimethyl- or diethyl-aniline to o-*isovaleryl*-p-*cresol* (p-*nitrophenylhydrazone*, orange-red, silky needles, m. p. 136—137°; *semicarbazone*, coarse needles or prisms, m. p. 203—204°, when rapidly heated). The identity of the ketone is established by its synthesis from *iso*valeryl chloride and *p*-tolyl methyl ether; it has b. p. 151°/21 mm., $D_4^{18 \cdot 4}$ 1·0291, D_4^{20} 1·028, $n_a^{18 \cdot 4}$ 1·52683, $n_D^{18 \cdot 4}$ 1·53270, $n_\beta^{18 \cdot 4}$ 1·55001, $n_\gamma^{18 \cdot 4}$ 1·56848, n_D^{20} 1·5320. *a-Bromo*-n-*butyrophenone*, colourless, mobile oil, b. p. 145—147°/14 mm., $D_4^{13 \cdot 25}$ 1·3724, D_4^{20} 1·364, $n_a^{13 \cdot 25}$ 1·55996, $n_D^{13 \cdot 25}$ 1·56520, $n_\beta^{13 \cdot 25}$ 1·58035, $n_\gamma^{13 \cdot 25}$ 1·59378, n_D^{20} 1·5622, is prepared from *a*-bromo-*n*-butyryl bromide, benzene, and aluminium chloride, and is converted by diethylaniline into *butyrophenone*, pale yellow oil, b. p. 120—125°/21 mm. (p-*nitrophenylhydrazone*, orange-red needles,

m. p. 161·5—162·5°). *α-Bromo*iso*butyrophenone* is a pale yellow oil, b. p. 135—137°/17 mm., $D_4^{14\cdot4}$ 1·3613, D_4^{20} 1·355, $n_\alpha^{14\cdot4}$ 1·55425, $n_D^{14\cdot4}$ 1·55923, $n_\beta^{14\cdot4}$ 1·57369, $n_\gamma^{14\cdot4}$ 1·58617, n_D^{20} 1·5567, which is transformed by diethylaniline into a mixture of approximately equal quantities of *iso*propyl- and *iso*propenyl-phenyl ketones. α-Bromo*iso*butyryl bromide reacts with *m*-5-xylenol methyl ether in the presence of aluminium chloride to yield 1:1:3:5-*tetramethylcoumaranone* and 2-iso*butyryl*-m-5-*xylenol*, m. p. 93—94°, the partial reduction of the brominated ketone primarily formed being effected by the liberated hydrogen bromide.

The conversion of α-bromo*iso*butyryl-*p*-cresol into *p*-cresotic acid by boiling pyridine has been previously described (Auwers, *loc. cit.*); the same acid is similarly obtained from the α-chloro-derivatives of *o*-propionyl-, *o*-butyryl-, and *o*-*iso*valeryl-*p*-cresol. Hydroxyl-free, halogenated ketones behave in the same manner; thus, benzoic acid is obtained from α-bromo-*n*-butyro- and α-bromo*iso*butyro-phenones. It appears possible that the first step in the action consists in the withdrawal of halogen acid from the compound, with the formation of a substance with an unsaturated side-chain; *p*-tolyl *iso*butenyl ketone is, however, unaffected by protracted boiling with pyridine. The action of quinoline differs from that of pyridine, since, for example, cresotic acid is not produced when it reacts with α-chloro*iso*valeryl-*p*-cresol; small quantities of 2:2:6-trimethylchromanone can, however, be isolated.

H. W.

The Reduction of Aromatic Ketones. W. D. Cohen (*Rec. trav. chim.*, 1920, **39**, 243—279).—It has previously been shown (A., 1919, i, 124, 210) that in acid solution, benzophenone is reduced, with the formation of benzopinacone, whilst in alkaline medium, benzhydrol is the product. When the reducing agent is aluminium amalgam, a mixture of the two is obtained, the amount of benzhydrol depending on the rate at which the pinacone is attacked, owing to the slightly alkaline reaction set up at the moment of reduction. It is now shown that in an absolutely neutral medium, the benzophenone being reduced in absolute alcohol by means of light, benzopinacone is the only product. The velocity of formation of benzopinacone under these conditions is proportional to the concentration of the alcohol and the amount of active light, but is independent of the concentration of the ketone. The thermal coefficient of this photochemical reaction is small, being about 1·1 for 10°. The velocity of the reaction depends to some extent on the character of the alcohol, but the nature of the ketone is the principal factor in directing the reaction. Substituted ketones are attacked less quickly than benzophenone itself. The relationships observed between the different ketones are independent of the alcohol used. This photochemical reduction of aromatic ketones by alcohols in sunlight is an irreversible reaction.

The actinic light is situated in the violet part of the visible spectrum, and probably in the neighbourhood of the rays 404·7 and 407·8 $\mu\mu$. The absorption of the ketones is selective. In a mixture of two ketones, one of them may absorb a part of the light necessary for the reduction of the other, and there may thus be a disturbance in the relative rates of reduction. W. G.

Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. V. *p*-Hydroxybenzophenones. P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 339—349. Compare A., 1917, i, 143).—4-Hydroxybenzophenone does not undergo any reduction when boiled with alcoholic potassium hydroxide even for six days, and the introduction of a chlorine or bromine atom into the para-position in the other nucleus has no influence.

4-Ethoxybenzophenone is slowly converted, under the same conditions, into 4-ethoxybenzhydrol, and the action is accelerated by the introduction of a chlorine or bromine atom into the *para*-position in the other nucleus. In this case, at the same time, a secondary reaction occurs, the chlorine or bromine becoming replaced by an ethoxy-group, giving 4 : 4′-diethoxybenzophenone.

The following new compounds are described: *4-chloro-4′-ethoxybenzophenone*, m. p. 121·25° (corr.), b. p. 223°/12 mm.; *4-chloro-4′-ethoxybenzhydrol*, m. p. 69·5° (corr.); *4 : 4′-diethoxybenzophenone*, m. p. 131·5° (corr.), b. p. 248°/15 mm.; *4-bromo-4′-ethoxybenzhydrol*, m. p. 80·5°. W. G.

Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. VI. Iodobenzophenones. P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 350—357. Compare preceding abstract).—Both 2-iodo- and 4-iodo-benzophenone are completely transformed into benzhydrol, the iodine being removed, when boiled with alcoholic potassium hydroxide. Under the same conditions, 3-iodobenzophenone is only partly converted into benzhydrol, part of it remaining unchanged. If an ethoxy-group is introduced into the iodobenzophenone, as in 4-iodo-4′-ethoxybenzophenone, the iodine is removed by boiling with alcoholic potassium hydroxide, but in this case the ethoxy-group exerts its influence in preventing the reduction, and the product is ethoxybenzophenone.

Chloro- and bromo-benzhydrols do not lose their halogen when boiled with alcoholic potassium hydroxide, but under similar conditions 4-iodobenzhydrol and, to a lesser extent, 3-iodobenzhydrol have their iodine removed.

m-Iodobenzoyl chloride condenses with benzene in sunlight in the presence of aluminium chloride to give *3-iodobenzophenone*, m. p. 42·5°, b. p. 226°/18 mm. It yields *3-iodobenzhydrol*, m. p. 54°. *4-Iodo-4′-ethoxybenzophenone*, m. p. 147·5°, b. p. 266°/17 mm., prepared from *p*-iodobenzoyl chloride and phenetole, gives *4-iodobenzhydrol*, m. p. 73°. W. G.

The Resin from Species of Xanthorrhœa not previously examined. EDWARD HENRY RENNIE, WILLIAM TERNENT COOKE, and HEDLEY HERBERT FINLAYSON (T., 1920, **117**, 338—350).

Glucosides. V. Synthesis of β-Gaultherin, of Methyl β-Tetra-acetylglucosidoanthranilate, and of β-Glucosido-resorcylic Acid Methyl Ether. P. KARRER and H. WEIDMANN (*Helv. Chim. Acta*, 1920, **3**, 252—257. Compare A., 1919, i, 594).—The action of diazomethane on an ice-cold alcoholic solution of glucosidosalicylic acid results in the formation of the *methyl* ester, $C_{14}H_{18}O_8$, associated with 1 mol. of alcohol of crystallisation, as leaflets, m. p. 90—92°, $[\alpha]_D^{15}$ −53·78° in alcohol. It is freed from alcohol by heating in a vacuum at 70°, and then has m. p. 105°. It gives no colour with ferric chloride and, whilst structurally identical with natural gaultherin, differs from it in that it is hydrolysed by emulsin, but not by gaultherase. Gaultherin is therefore the α-stereoisomeride. The *tetra-acetyl* derivative of the above ester, $C_{22}H_{26}O_{12}$, needles, m. p. 154°, $[\alpha]_D^{13}$ −44·77° in chloroform, is identical with Mauthner's product (A., 1918, i, 544), which therefore is not tetra-acetyl gaultherin. *Methyl β-tetra-acetyl-glucosidoanthranilate*, $C_{22}H_{27}O_{11}N$, prepared from the acid by treatment with diazomethane, forms needles, m. p. 165°, $[\alpha]_D$ −54·88° in chloroform. *β-Tetra-acetyl glucosido-4-methoxysalicylic acid*,

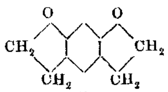
$C_{22}H_{26}O_{13}$,

m. p. 160°, $[\alpha]_D^{15}$ −48·81° in alcohol, is obtained by condensation of silver 4-methoxysalicylate with acetobromoglucose. It gives no colour with ferric chloride. By hydrolysis with cold baryta it yields *β-d-glucosido-4-methoxysalicylic acid*, needles, m. p. 163°, $[\alpha]_D^{1}$ −81·55° in water. It is hydrolysed by emulsin, and gives no colour with ferric chloride. The *tetra-acetylglucose* ester of *4-methoxy-salicylic acid*, $C_{22}H_{26}O_{13}$, is also produced in the above condensation. It forms needles, m. p. 147°, $[\alpha]_D^{16}$ −45·37° in chloroform. J. K.

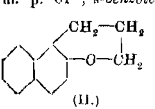
Syntheses of Chromans [Benzopyrans] and Coumarans. II. R. E. RINDFUSZ, P. M. GINNINGS, and V. L. HARNACK (*J. Amer. Chem. Soc.*, 1920, **42**, 157—165).—The methods described previously (A., 1919, i, 342) have been applied to substituted phenols. In general, it is found that the dehydration of hydroxyethyl and hydroxypropyl phenyl ethers can be effected more conveniently with phosphoric oxide than with zinc chloride. The procedure consists in boiling the mixture of reagents for about an hour in the presence of an inert solvent (such as toluene or methyl ethyl ketone), the boiling point of which is such as to allow a fairly high temperature being attained without, however, rendering the subsequent fractionation of the product a matter of difficulty.

The following compounds are described: *o-tolyl γ-hydroxypropyl ether*, b. p. 174—176°/42 mm., D^{29} 1·053, n_D^{29} 1·523; *o-tolyl γ-bromo-propyl ether*, b. p. 154—156°/20 mm., D^{29} 1·299, n_D^{29} 1·535; *8-methyl-benzopyran*, b. p. 114—116°/20 mm., D^{29} 1·039, n_D^{29} 1·542; *o-tolyl β-hydroxyethyl ether*, b. p. 143—145°/20 mm., D^{29} 1·079, n_D^{29} 1·528;

o-tolyl β-bromoethyl ether, b. p. 133—134°/20 mm., D^{29} 1·360, $n_D^{?}$ 1·544; *6-methylcoumaran*, b. p. 119—120°/65 mm., D^{29} 1·0?0, $n_D^{?}$ 1·527; *p-bromophenyl γ-hydroxypropyl ether*, b. p. 206°/48 mm., D^{24} 1·442, $n_D^{?}$ 1·563; *6-bromobenzopyran*, b. p. 143—144°/18 mm., D^{25} 1·465, $n_D^{?}$ 1·580; *p-bromophenyl β-bromoethyl ether*, b. p. 165°/16 mm., m. p 56°; *4-bromocoumaran*, b. p. 135°/20 mm. D^{20} 1·436, $n_D^{?}$ 1·555; *p-bromophenyl β-hydroxyethyl ether*, b. p. 184°/20 mm., m. p. 49—50°; *m-phenylene di-β hydroxyethyl ether*, $C_6H_4(O{\cdot}CH_2{\cdot}CH_2{\cdot}OH)_2$, b. p. 230—234°/30 mm. m. p. 81°; *s-benzotetrahydrodifuran* (formula I), b. p. 110—113° 148 mm., D^{25} 0·861, $n_D^{?}$ 1·448; *m-phenylene di γ-hydroxypropyl ether*, b. p. 246—248°/20 mm. D^{31} 1·145, $n_D^{?}$ 1·529; *s-benzotetrahydrodipyran* b. p. 97°/75 mm., $n_D^{?}$ 1·448; *β-naphthyl γ-hydroxypropyl ether*, m. p. 99—99·5°; *β-naphthadihydropyran* (formula II), m. p. 41—42° *β-naphthyl β-hydroxyethyl ether*, m. p. 76—77° *β-naphthadihydrofuran*, b. p. 185°/10 mm. (some decomp.), D^{30} 1·006($n_D^{?}$ 1·482; *β-naphthyl β-bromoethyl ether*, m. p. 91·5—92·5°. H. W.



(I.)



(II.)

Synthesis of Acids by the Action of Acid Anhydrides o Alcohols containing a Pyran Ring. Replacement of th Hydroxyl by the Group $\cdot CH_2\cdot CO_2H$ or the Group $\cdot CHR\cdot CO_2H$ R. Fosse (*Ann. Chim.*, 1920, [ix], **13**, 87—104).—A full accoun of work already published (compare A., 1906, i, 691). W. G.

Constitution of Ephedrine. Deoxyephedrine. A. Ogat (*J. Pharm. Soc. Japan*, 1919, **451**, 751—764).—By a compariso of the physical constants of the two bases and of their salts, th author shows that deoxyephedrine is identical with *d*-β-phenylis propylmethylamine, prepared by reducing with sodium and alcoh the condensation product obtained by keeping a mixture of benz methyl ketone and alcoholic methylamine for four weeks, ar resolving the racemic base obtained with tartaric acid. Cons quently, ephedrine has the constitution OH·CHPh·CHMe·NHMe Chemical Abstracts.

Metallic Salts of Pyrrole, Indole, and Carbazole. Edward Franklin (*J. Physical Chem.*, 1920, **24**, 81—99).—The "ammon acids" (compare A., 1905, i, 582; 1912, ii, 437), pyrrole, indo and carbazole, have been converted into their metallic salts by t action of metals (sodium, potassium, magnesium, or calcium) or t metal amides (sodium, potassium, silver) on solution of t "ammono-acids" in liquid ammonia. In the case of pyrrole, crystalline potassium salt could not be obtained, and on evaporati the solution an amorphous, viscous mass was always produc Sodium forms a crystalline compound with pyrrole, C_4H_4NNa,NH on cooling the solution to the temperature produced by solid carb dioxide and ether. This compound loses ammonia at 20° and yie the compound, C_4H_4NNa; it is hydrolysed by water, yielding pyrr

and sodium hydroxide. *Calcium pyrrole*, $(C_4H_4N)_2Ca,4NH_3$, forms colourless crystals, but on losing its ammonia to form the "anammonous" salt it becomes slightly yellow, and has the dull appearance of an effloresced salt. It is vigorously attacked by water and pyrrole and calcium hydroxide are formed. In the preparation from metallic calcium it is shown that there is a deficiency in the hydrogen evolved which is due to the formation of a small amount of tetrahydropyrrole. *Magnesium pyrrole*, $(C_4H_4N)_2Mg,2NH_3$, forms colourless crystals. *Silver pyrrole*, C_4H_4NAg,NH_3, is a well-crystallised product, which on keeping rapidly turns grey, and finally becomes black. The sodium and potassium salts of indole both form amorphous, viscous masses, from which it was not possible to obtain crystals. *Calcium indole*, $(C_8H_6N)_2Ca,4NH_3$, forms beautiful, white crystals, which on heating to 100° decompose into indole and calcium amide. In the preparation about one-half of the indole was reduced to dihydroindole. *Magnesium indole*,

$$(C_8H_6N)_2Mg,4NH_3,$$

forms needle-shaped, colourless crystals which, although quite soluble in liquid ammonia when freshly prepared, after a time are not completely soluble. This is probably due to a decomposition with the formation of an insoluble product. *Silver indole*, C_8H_6NAg,NH_3, is an extremely soluble, crystalline compound which exhibits the phenomenon of supersaturation to a marked degree. *Potassium carbazoles*, $C_{12}H_8NK,2NH_3$ and $C_{12}H_8NK,NH_3$, form very soluble crystals, which lose their ammonia at 20°. *Silver carbazole*, $C_{12}H_8NAg,2NH_3$, is formed at −39°, and on warming loses one molecule of ammonia to give $C_{12}H_8NAg,NH_3$. *Calcium carbazole*, $(C_{12}H_8N)_2Ca,7NH_3$, forms yellow crystals with a green fluorescence at −39°, and on heating at 30° loses three molecules of ammonia to give $(C_{12}H_8N)_2Ca,4NH_3$. J. F. S.

Pyrrole-blacks. A. Angeli and Corrado Lutri (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 14—22. Compare A., 1919, i, 134).—In presence of water, pyrrole and *p*-benzoquinone rapidly react, giving first a reddish-brown, colloidal solution clearly showing Tyndall's phenomenon and then a black, amorphous powder closely resembling pyrrole-blacks and melanins; the mother liquor contains considerable proportions of quinol. The reaction takes place also in alcoholic, ethereal, or, more slowly, moist benzene solution. If the product of the reaction is washed with water and extracted with alcohol in a reflux apparatus, a black substance is obtained which, when heated, does not melt, but emits vapour which colours red a pine splinter moistened with hydrochloric acid; it dissolves in alkali hydroxide solution, giving an intense brownish-black coloration, but is insoluble in alkali carbonate solution. The percentage compositions of two preparations are: C, 69·14—69·22 (68·75—68·85); H, 2·86—2·90 (2·80—2·84); N, 6·11 (—), and the compound is probably formed by the interaction of 3 mols. and 5 mols., or 4 mols. and 7 mols., of pyrrole and *p*-benzoquinone respectively. The conclusion is drawn that the melanins represent complex molecules

similar to the polysaccharides, polypeptides, polyterpenes, caoutchouc, etc., the tendency to polymerise being due partly to the presence of conjugated double linkings in the pyrrole molecule. Under the same conditions indole does not react with pyrrole.

Similarly, pyrrole and 1:4-naphthaquinone interact, yielding naphthaquinol and a *compound*, $C_{34}H_{19}O_5N$ (?), which crystallises in violet-black needles and, when heated, melts incipiently and at the same time emits vapour giving a red coloration to a pine splinter moistened with hydrochloric acid; it is readily decomposed by hot potassium hydroxide solution with formation of an orange-coloured product very sparingly soluble in the ordinary solvents. The compound appears to be formed by the condensation of 1 mol. of pyrrole with 3 mols. of the naphthaquinone.

Isatin and pyrrole also react readily (compare Liebermann and Kraus, A., 1907, i, 657).

Oxidation of pyrrole by means of hydrogen peroxide yields (1) a pyrrole black, and (2) a *compound*, $C_8H_{10}ON_2$, which crystallises in shining, almost colourless needles, m. p. 136°, and at about 200° in presence of air blackens and emits vapour giving an intense red coloration to a pine splinter moistened with hydrochloric acid. By a few drops of dilute sulphuric acid and a trace of dichromate this compound is coloured brown, a black powder being slowly deposited. With nitrous acid or ferric chloride it gives a yellow coloration and, later, a black powder. With a trace of nitroprusside and potassium hydroxide it yields a brilliant violet coloration turned deep blue by acetic acid. T. H. P.

Benzidino-quinones and Bisquinonylbenzidines as Vat Dyes. KURT BRASS and OTTO PAPP (*Ber.*, 1920, **53**, [*B*], 446—462). —Previous attempts to study the primary product of the interaction of benzidine on *p*-benzoquinone (Brass, A., 1913, i, 1232) were rendered difficult on account of the readiness with which it loses a molecule of benzidine to yield quinonebenzidine, which is subsequently readily polymerised. More successful attempts are now described in which substituted quinones are employed.

Benzidino-toluquinone is prepared by the action of a solution of benzidine in 50% acetic acid on a hot aqueous solution of toluquinone; it forms a dark violet powder, which is decomposed by prolonged contact with air. By reduction with hyposulphite in very faintly alkaline solution, it yields a yellow vat, from which cotton is dyed in brown shades, which, however, are due to the polymerised form of the dye. The free amino-group shows little tendency to enter into action, but its presence is established by the isolation of N-p-*chlorobenzylidenebenzidino-toluquinone*,

$$C_6H_2O_2Me\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N{:}CH\cdot C_6H_4Cl.$$

Methylanilino-*p*-benzoquinone condenses with benzidine in alcoholic solution to yield a mixture of 2-benzidino-5-methylanilinobenzoquinone, m. p. 216—217° (corr.) [H. and W. Suida, A., 1919, i, 81, give 215—218°], and relatively small amounts of NN′-*bis*-5-*methylanilinobenzoquinonyl*-2-*benzidine*, $[NMePh\cdot C_6H_2O_2\cdot NH\cdot C_6H_4-]_2$,

m. p. 254° (decomp.). The substances have similar tinctorial properties, and dye cotton in yellowish-brown shades from a yellow vat. *2-Di-o-anisidino-5-methylanilinobenzoquinone*,

$$NMePh{\cdot}C_6H_2O_2{\cdot}NH{\cdot}C_6H_3(OMe){\cdot}C_6H_3(OMe){\cdot}NH_2,$$

brown leaflets, m. p. 124—128° (decomp.) after softening from 120°, and *NN′-bis-5-methylanilinobenzoquinonyl-2-dianisidine*, $[NMePh{\cdot}C_6H_2O_2{\cdot}NH{\cdot}C_6H_3(OMe)-]_2$, brown needles, m. p. 244—246° (corr.), are prepared from methylanilinobenzoquinone and di-o-anisidine, and are separated by taking advantage of the greater solubility of the latter in acetone; on cotton, they yield brown shades with a tendency towards olive.

Another ready method of preparing simple vat dyes consists in the oxidation of anilino-quinones to benzidine derivatives (compare Brass, A., 1912, i, 874); 2-anilino-3:5:6-trichlorobenzoquinone, however, is converted by manganese dioxide in the presence of sulphuric acid into *3′-anilino-2′:5′:3:5:6-pentachlorodibenzoquinonylaniline*, $C_6O_2Cl_3{\cdot}NPh{\cdot}C_6O_2Cl_2{\cdot}NHPh$, microcrystalline, bluish-grey leaflets, which does not melt below 300° and dyes cotton in dull brown shades.

Whilst benzidine and α-naphthaquinone yield only 2-benzidino-α-naphthaquinone (Pummerer and Brass, A., 1911, i, 655), it is found that dianisidine, under similar conditions, gives *NN′-bis-α-naphthaquinonyl-2-dianisidine*, $[C_{10}H_5O_2{\cdot}NH{\cdot}C_6H_3(OMe)-]_2$, brownish-violet, crystalline powder, m. p. 303—305°, which dyes cotton in violet shades. In a similar manner, *NN′-bis-3-chloro-α-naphthaquinonyl-2-dianisidine*, red needles, m. p. 270—272°, is prepared from 2:3-dichloro-α-naphthaquinone; it gives brownish-violet shades on cotton. o-Ethoxybenzidine and α-naphthaquinone yield *NN′-bis-α-naphthaquinonyl-3-ethoxybenzidine*,

$$C_{10}H_5O_2{\cdot}NH{\cdot}C_6H_3(OEt){\cdot}C_6H_4{\cdot}NH{\cdot}C_{10}H_5O_2,$$

slender, violet-brown needles, m. p. 279—281°, which dyes cotton in violet shades. H. W.

Four-membered Cyclic Ureas. III. Condensation of *iso*Cyanic Acid with Alkyl Schiff Bases and Related Compounds. William J. Hale and Norbert A. Lange (*J. Amer. Chem. Soc.*, 1920, **42**, 107—116).—Further investigation shows that the condensation of *iso*cyanic acid with Schiff bases which contain an alkyl group attached to the nitrogen atom proceeds in the same manner as with benzylidene-ethylamine (A., 1919, i, 225). The reaction has been further extended to substances which contain the carbimino-nucleus attached to a nitrogen atom, and, in the special instance of benzylbenzylidenehydrazone,

$$CHPh{:}N{\cdot}NH{\cdot}CH_2Ph,$$

the results obtained confirm those of Bailey and Moore (A., 1917, i, 355).

4:6-Diketo-2-phenyl-1-propylhexahydro-1:3:5-triazine,

$$CHPh{<}{}^{NPr\cdot CO}_{NH-CO}{>}NH,$$

colourless, flaky needles, m. p. 211°, is prepared by the gradual

addition of powdered potassium cyanate to a well-cooled solution of benzylidene-*n*-propylamine in glacial acetic acid; the corresponding *monoacetyl* derivative forms colourless prisms, m. p. 120°. 4 : 6-*Di-keto-2-phenyl-1-butylhexahydro-1 : 3 : 5-triazine* is prepared in a similar manner and has m. p. 188°, whilst 4 : 6-*diketo-2-phenyl-1-amylhexahydro-1 : 3 : 5-triazine* has m. p. 202°.

Benzylbenzylidenesemicarbazone (Bailey and Moore, *loc. cit.*) is *slowly hydrolysed when treated with steam in the presence of hydro*chloric acid to benzaldehyde and benzylhydrazine hydrochloride, the action proceeding as indicated by the scheme:

$$CH_2Ph\cdot N(CO\cdot NH_2)\cdot N{:}CHPh \longrightarrow CH_2Ph\cdot N(CO\cdot NH_2)\cdot NH_2 \longrightarrow CH_2Ph\cdot NH\cdot NH_2.$$

A mixture of 2-benzylsemicarbazide, $CH_2Ph\cdot N(CO\cdot NH_2)\cdot NH_2$, m. p. 135—136°, and 1-benzylsemicarbazide,

$$CH_2Ph\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

m. p. 155°, is obtained by the cautious addition of potassium cyanate to a concentrated, ice-cold, aqueous solution of benzylhydrazine hydrochloride; the two substances are readily separated by taking advantage of the sparing solubility of the latter in cold chloroform, in which the former is freely soluble (compare Curtius, A., 1910, i, 610; Busch, Opfermann, and Walther, A., 1904, i, 628; Kessler and Rupe, A., 1912, i, 219). The 2-derivative is smoothly transformed into the 1-compound when heated for a few minutes at its melting point.

as-Diphenylbenzylidenehydrazine, $CHPh{:}N\cdot NPh_2$, phenylbenzylidenehydrazine, and 2-benzyl-1-benzylidenesemicarbazone could not be caused to condense with *iso*cyanic acid. H. W.

Origin of the Humin formed by the Acid Hydrolysis of Proteins. IV. Hydrolysis in the Presence of Aldehydes. III. Comparative Hydrolysis of Fibrin and Gelatin in the Presence of Various Aldehydes. GEORGE E. HOLM and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1920, **42**, 632—640).—Previous work on the influence of the presence of aldehydes on the nature of the products obtained by acid hydrolysis of proteins (A., 1918, i, 84) has been extended by the hydrolysis of fibrin and gelatin in presence of benzaldehyde, acetaldehyde, butaldehyde, and *iso*butaldehyde. Whilst the proportions of "ammonia" and soluble humin nitrogen are not appreciably altered, that of acid-insoluble humin nitrogen increases rapidly to a maximum with increase in the quantity of benzaldehyde used. This result is ascribed to the presence of both tryptophan and tyrosine. Butaldehyde and *iso*butaldehyde are similar in their effects to benzaldehyde, but they give rise to black, insoluble residues, possibly the result of their polymerisation. This change is much more marked in the case of Macetaldehyde, and consistent results are therefore not obtained. solWhilst the total amino-nitrogen in the filtrate from the soluble quintin diminishes rapidly when hydrolysis is carried out in presence give 2creasing amounts of formaldehyde, probably owing to condensa-*anilino*of formaldehyde with amino-acids, only a slight decrease is

observed when benzaldehyde, or butaldehyde, or *iso*butaldehyde is used. J. K.

Distribution of Basic Nitrogen in Phaseolin. A. J. FINKS and CARL O. JOHNS (*J. Biol. Chem.*, 1920, **41**, 375—377).—The average values are: cystine, 0·84%; arginine, 6·11%; histidine, 3·32%, and lysine, 7·88%. The latter value is considerably higher than that obtained by the direct method of Kossel and Patten (A., 1903, ii, 582). J. C. D.

Effect of Poisons on an Enzymatic Process. V. Alkaloids, Caffeine. C. G. SANTESSON (*Skand. Arch. Physiol.*, 1919, **39**, 132—166; from *Chem. Zentr.*, 1920, i, 392. Compare A., 1915, i, 728).—In continuation of previous investigations, the influence of the following substances on the power of the catalase of frog's muscle to effect the decomposition of hydrogen peroxide has been studied: pyridine, quinoline, quinine, quinine hydrochloride and hydrobromide, veratrine, veratrine hydrochloride, caffeine, nicotine and its hydrochloride, veratrine (Swedish pharmacopœia), coniine and its hydrochloride, morphine and its hydrochloride, dionine, diacetylmorphine (base and hydrochloride), cocaine (base and hydrochloride), atropine (base and sulphate), strychnine, and aconitine (base and acid hydrochloride). The majority of the free alkaloids, even in very dilute solution, facilitate the action of the catalase to a marked degree, and a similar effect is observed with pyridine; little or no activation is observed only with quinoline, coniine, and caffeine. The alkaloidal salts, on the other hand, generally have a restraining action; nicotine hydrochloride, ethylmorphine (dionine), and atropine sulphate are exceptions in this respect. H. W.

Composition of Salvarsan. ROBERT GEORGE FARGHER and FRANK LEE PYMAN (T., 1920, **117**, 370—377).

Silver Salvarsan. A. BINZ, H. BAUER, and A. HALLSTEIN (*Ber.*, 1920, **53**, [*B*], 416—428).—From a study of silver salvarsan and allied substances, the authors are led to the following conclusions: (1) colloidal silver is not present in silver salvarsan; (2) two molecules of silver nitrate react with one molecule of salvarsan or its derivative; (3) silver salvarsan contains silver oxide in complex form; (4) Karrer's hypothesis that the silver atoms are united by the residual affinities of the arsenic atoms is not established, since this would indicate a tendency for the latter to pass into the quinquevalent state, whereby they would lose therapeutic power; probably the amino-groups, the capacity of which to take part in complex salt formation is well established, are responsible for the formation of metallic derivatives, or, as recently suggested by Dilthey, the metallic atoms may be united to the molecule as a whole, and not to any particular group.

3-Amino-4-hydroxyphenylarsinic acid is diazotised and converted into 3-chloro-4-hydroxyphenylarsinic acid, which, on nitration, yields 3-chloro-5-nitro-4-hydroxyphenylarsinic acid; the latter is

reduced by hyposulphite to 5:5′-dichloro-3:3′-diamino-4:4′-dihydroxyarsenobenzene, the *dihydrochloride* of which,

$$C_{12}H_{10}O_2N_2Cl_2As_2,2HCl,2MeOH,$$

forms greenish-yellow flocks, and is transformed by silver nitrate into *dichlorosalvarsan di-silver chloride*,

$$As_2[C_6H_2Cl(OH)\cdot NH_2]_2,2AgCl,$$

yellow, gelatinous precipitate. The corresponding copper salt, $As_2[C_6H_2Cl(NH_2)\cdot O\,cu]_2CuCl_2$, is yellowish-brown.

3:3′-*Diamino-4:4′-dihydroxyarsenobenzene di-silver iodide*, $As_2[C_6H_3(NH_2)\cdot OH]_2,2AgI$, is prepared by successive treatment of an aqueous solution of the salvarsan base with hydriodic acid and silver nitrate, and forms an orange-coloured colloidal precipitate. Attempts to convert it into the silver salvarsan base,

$$As_2[C_6H_3(NH_2)\cdot OH]_2,Ag_2O,$$

by means of sodium carbonate were not completely successful, since oxidation occurred during the washing of the primary black precipitate. When treated with sodium hydroxide, it gives the soluble sodium salt of silver salvarsan, in which the absence of colloidal silver or silver oxide is demonstrated by ultra-filtration experiments, by the absence of the Tyndall phenomenon, and by the appearance under the ultramicroscope. When copper chloride and salvarsan are mixed in aqueous solution, a yellow precipitate of 3:3′-*diamino-4:4′-dihydroxyarsenobenzene mono-copper chloride hydrochloride*, $As_2[C_6H_3(OH)\cdot NH_2]_2,CuCl_2,HCl$, is obtained.

3:5:3′:5′-Tetrabromo-*p*-arsenophenol is mainly oxidised by silver nitrate in pyridine methyl-alcoholic solution, yielding, amongst other products, the *substance*,

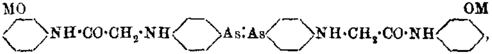
$$AgO\cdot C_6H_2Br_2\cdot AsO_3H_2,C_5H_5N,$$

m. p. 157—158°, in which the relative positions of pyridine and silver may possibly be reversed. When a solution of the sodium salt of 3:5:3′:5′-tetrabromo-*p*-arsenophenol is treated with silver nitrate, it gives a brown precipitate of *di-silver 3:5:3′:5′-tetrabromo-p-arsenophenoxide*, which dissolves in sodium hydroxide to a clear brown solution which closely resembles sodium silver salvarsan, but, on ultra-filtration, gives a black residue of colloidal silver and a colourless solution.

Arsenobenzene, conveniently prepared by the reduction of phenylarsinic acid with hypophosphorous acid, has m. p. 208°, whereas Michaelis and Schulte give m. p. 196°. When treated with silver nitrate, it becomes coated with a brownish-black deposit of silver, and is partly transformed into phenylarsinic acid; a somewhat similar phenomenon is observed with gold chloride, but it does not appear to react with copper chloride. H. W.

Aromatic Arsenical Compounds. Walter Abraham Jacobs, Wade Hamilton Brown, Michael Heidelberger, and Louise Pearce (Brit. Pat. 128181; addition to Brit. Pat. 120385. Compare A., 1919, i, 231).—The sodium or potassium salts of the

N-(arsenoaryl)bis-α-aminoacylarylamides of the formula



where M is the alkali metal, previously described (*loc. cit.*), are equally valuable for the treatment of trypanosomal or spirochætal infection, and, being soluble in water, are particularly suitable for practical therapeutic use. As an example of their preparation, equivalent quantities of sodium hydroxide and *N*-(arsenophenyl)-bisglycyl-*m*-aminophenol may be dissolved together in water, and the salt isolated either by evaporating to dryness under reduced pressure or by precipitation with a liquid miscible with water, such as acetone or alcohol. It forms a yellow powder, readily soluble in water. G. F. M.

Physiological Chemistry.

The Equilibrium between Oxygen and Carbonic Acid in Blood. LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1920, **41**, 401—430).—This paper seeks to explain the interaction between oxygen and carbonic acid in blood by means of the theory of acid-base equilibrium. The isohydric change from fully reduced to fully oxygenated blood, the transfer of base from carbonic acid to hæmoglobin, which is the main feature of this process, and the change of strength, as acid, of a portion of the hæmoglobin molecule, which is its cause, are discussed. It is shown that all these phenomena can be explained by the assumption that a certain acid radicle of the hæmoglobin molecule has, for reduced hæmoglobin and oxyhæmoglobin, respectively, the following values: $K_R = 2{\cdot}3 \times 10^{-8}$, $K_0 = 2{\cdot}0 \times 10^{-7}$. From this consideration, it follows that the salt of the acid radicle in question must have a greater affinity for oxygen than the free acid. If the mass law constants of the reaction of salt and acid with oxygen were K_s and K_A, respectively, it should be approximately true that $K_A/K_s = K_0/K_R = 9$. In the light of these considerations, the equilibrium between protein acid radicles and base in blood is examined. The bearings of these considerations on Hill's equation for the equilibrium between hæmoglobin and oxygen is considered, but at this point the difficulties are only partly overcome. The union of hæmoglobin as a base with acids, and especially with carbonic acid in blood, is discussed. Finally, the bearing of these considerations on the physiological processes, both the homogeneous reactions within the corpuscles and the plasma, and also the heterogeneous exchanges between corpuscles and plasma, is investigated. J. C. D.

Alkalinity of Blood. René Clogne (*J. Pharm. Chim.*, 1920, [vii], **21**, 49—62).—See this vol., ii, 340.

The Colloidal Chemical Action of Normal Alkali Salts on the Process of Phagocytosis. W. Radsma (*Arch. Néerland Physiol.*, 1920, **4**, 197—215).—The influence of normal alkali salts on phagocytosis depends both on the cations and the anions. Arranged in descending order of intensity of phagocytosis, the anions are Cl′, ClO_3', Br′, NO_3', I′, CNS′, and the cations are Na˙, K˙, Rb˙, Cs˙, Li˙, there being very little difference between corresponding salts of sodium, potassium, and rubidium. The action of these salts on the process of phagocytosis must be considered as a lyotropic action. The compounds formed between the protein substances of the protoplasm of the membrane of the leucocytes and the ions mentioned above play no direct part in the mechanism of phagocytosis. The point of action of the salt is not at the interior of the leucocyte, but in the protein substances at the surface of the leucocyte, and the intensity of the phagocytosis is an indicator of the colloidal chemical structure of the protein substances of the protoplasm at this surface. W. G.

Nutritive Value of the Proteins of the Barley, Oat, Rye, and Wheat Kernels. Thomas B. Osborne and Lafayette B. Mendel [with the co-operation of Alfred J. Wakeman] (*J. Biol. Chem.*, 1920, **41**, 275—306).—The proteins of the entire kernel of these grains are adequate for the growth of albino rats, being more efficient for this purpose than the proteins of the endosperm alone. J. C. D.

Studies in Nutrition. II. The Rôle of Cystine in Nutrition as Exemplified by Nutrition Experiments with the Proteins of the Navy Bean (Phaseolus vulgaris). Carl O. Johns and A. J. Finks (*J. Biol. Chem.*, 1920, **41**, 379—389).—Cystine is essential for normal growth. Phaseolin, the principal protein of the navy bean, is rendered a more efficient food by heating with water. Cooked phaseolin or cooked navy bean, when supplemented with cystine, furnished adequate protein for normal growth. J. C. D.

The Influence of Radioactive Elements on the Development [of Tadpoles]. A. J. P. van den Broek (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 563—567).—Tadpoles in a medium containing a radioactive substance antagonistic to potassium, namely, uranium, grow and metamorphose less quickly than in a medium only containing potassium. There is an indication that the presence of equi-radioactive quantities of the antagonistic substance tends to prevent the absorption of potassium by the tadpole, and there is also some indication of a poisoning effect. W. G.

Effect of the Chlorine Substitution Products of Methane, Acetaldehyde, and of Sodium Acetate on Catalase Production. W. E. BURGE and F. L. BURGE (*J. Biol. Chem.*, 1920, **41**, 307—314).—The inhibitory action of chlorine substitution products of methane on catalase action is proportionate to the degree of substitution. Similarly, chloral is more inhibitory than acetaldehyde. The ingestion of sodium acetate causes an increase of catalase, but this is less marked when sodium salts of the chloroacetic acids are used. The chlorine appears to decrease catalase by direct destruction and by decreasing the output from the liver. The increase in oxidation following the ingestion of glycine is attributed to an increase in catalase, whereas the decrease in oxidation during narcosis is attributed to a decrease in the enzyme.

J. C. D.

Influence of Uranium and Potassium on the Viscosity of Colloidal Liquids. I. GUNZBURG (*Arch. Néerland. Physiol.*, 1920, **4**, 233–242).—The viscosity of the muscular juice from a frog is above normal in liquids containing less than 25 mg. or more than 100 mg. of uranyl nitrate per litre, there being a point of minimum viscosity at a concentration of approximately 50 mg. of uranyl nitrate per litre. In the presence of potassium chloride, the viscosity remains almost constant at a value below normal for all concentrations of the chloride, although there is indication of a critical point at a concentration of 0·75—1·25 grams of potassium chloride per litre. In the presence of a mixture of the two salts, the viscosity of the muscular juice depends on the relative proportions of the two salts present.

W. G.

Genesis of Thiocyanic Acid in Animals. IX. SERAFINO DEZANI (*Arch. Farm. sperim. Sci. aff.*, 1919, **28**, 23—32. Compare this vol., i, 345).—The results of further experiments, together with those already described, lead to the final conclusion that thiocyanic acid is not produced in the animal organism, but is purely exogenetic.

T. H. P.

Chemistry of Vegetable Physiology and Agriculture

Biochemistry of the Acetone and Butyl Alcohol Fermentation of Starch by Bacillus Granulobacter Pectinovorum. HORACE B. SPEAKMAN (*J. Biol. Chem.*, 1920, **41**, 319—343).—*Bacillus granulobacter pectinovorum* growing in a medium rich in starch changes the latter into dextrose by exoenzymic activity. The dextrose then passes into the cell, and is oxidised to acetic and butyric acids, which are reduced in part to the corresponding alcohols.

J. C. D.

Fermentation of Lævulose by Lactobacillus pentoaceticus, N. Sp. W. H. Peterson and E. B. Fred (*J. Biol. Chem.*, 1920, **41**, 431—450).—These organisms, which are closely related to the so-called "mannitol bacteria," will attack lævulose, with the production of acetic and lactic acids, mannitol, and carbon dioxide. As much as 30 to 40% of the lævulose may be converted into mannitol in the early stages of the fermentation, but if the process is allowed to go on for a long time, this product is slowly attacked, with the formation of acetic and lactic acids. The same organisms will decompose calcium and sodium malates, with the formation of carbon dioxide and lactic and acetic acids. It is suggested that malic acid may be an intermediate product in the fermentation of the lævulose. J. C. D.

Chemistry of Alcoholic Fermentation. Carl Neuberg and Elsa Reinfurth (*Ber.*, 1920, **53**, [*B*], 462—469).—The results obtained recently by Zerner (this vol., i, 350) are in general agreement with the older data of Neuberg and his co-workers. Zerner, however, attributes the impossibility of effecting complete conversion of sugar into glycerol and acetaldehyde to a comparatively slow union of the latter with the bisulphite; the work of Kerp shows, on the other hand, that the union is rapid, whilst, in addition, the importance of the development of alkali hydroxide ($Me\cdot CHO + Na_2SO_3 + H_2O = Me\cdot CH(OH)\cdot O\cdot SO_2Na + NaOH$) has been completely overlooked. Further, Zerner's conclusion that pyruvic acid cannot be the preliminary stage in the formation of acetaldehyde is based on an erroneous interpretation of an unsuitably devised experiment; absence of evolution of carbon dioxide from a fermenting solution of potassium pyruvate in the presence of a molecule of normal sodium sulphite is to be expected, since reaction occurs in accordance with the scheme $COMe\cdot CO_2K + Na_2SO_3 + H_2O \longrightarrow OH\cdot CHMe\cdot O\cdot SO_2K + Na_2CO_3$. The action is also complicated by the fact that fermentation occurs within the living yeast cell, which is now shown to be impermeable to normal sodium sulphite, so that the union of the latter with the aldehyde must occur outside the cell. H. W.

The Biochemical Production of Pyruvic Acid. A. Fernbach and M. Schoen (*Compt. rend.*, 1920, **170**, 764—766. Compare A., 1913, i, 231; 1914, i, 237, 910).—Further evidence is given of the formation of pyruvic acid by yeast during alcoholic fermentation. An essential condition for its production is that the medium should be kept neutral, which is best done by the addition of calcium carbonate. Thus, by a change in the reaction of the medium, a change is produced in the nature and relative proportions of the products formed. The formation of pyruvic acid also requires that the medium shall be an inorganic one. W. G.

The Significance of the Peroxydase Reaction with Reference to the Viability of Seeds. J. S. McHargue (*J. Amer. Chem. Soc.*, 1920, **42**, 612—615).—Although it has been suggested

that tissues or organs are dead if they fail to show the reactions of peroxydases and oxydases, the author has observed that dead grains, for example, lettuce seed, which failed to give the former reaction, contained a catalase which decomposed hydrogen peroxide; but evidence is adduced to show that the peroxydase reaction is only given by viable seed, and that the intensity of the reaction can be used to distinguish between seeds of low, medium, and high viability. The reaction failed with samples of corn, hemp seed, tomato seed, tobacco seed, oats, cowpeas, soja beans, castor beans, and lettuce seed, which all showed zero germination. Moreover, the temperature at which the blue colour disappeared increased with viability of the seed, although it varied somewhat with the species. Further, the peroxydase reaction was given by the germ, but not by the endosperm, of corn; but when the separation and grinding preparatory to the test were performed under water or alcohol, the germs also gave only a faint reaction, showing that they contain a substance, presumably an oxygenase, which, on exposure to air, rapidly absorbs oxygen, forming the peroxydase. Of the twenty species examined, only soja beans, lucerne, and lettuce seeds contained both oxydases and peroxydases; the respective reactions in each case were both pronounced, weak and strong, intense and moderate. J. K.

Carbon Monoxide a Product of Respiration. SETH C. LANGDON and WALTER R. GAILEY (*J. Amer. Chem. Soc.*, 1920, **42**, 641—646).—The conditions under which carbon monoxide is produced in the pneumatocyst (floater) of the giant Pacific Coast kelp, *Nereocystis leutkeana* (A., 1917, i, 372), have been more closely examined. It is not a result of decay or due to the action of enzymes, because finely ground kelp in contact with sea-water gives carbon dioxide and hydrogen only. When the lower part of the stipe was cut away, and the upper part closed with a cork and suspended in the sea after being filled with a gas of known composition, the plant continued to live and grow. When air was used, carbon monoxide was produced, irrespective of whether the fronds had been removed or not, or whether the plant was kept in the light or in the dark, and whatever sections of the stipe were employed. With nitrogen or hydrogen, however, no carbon monoxide was produced, but several per cent. of carbon dioxide were produced. Finally, carbon monoxide was only generated in the living plant. It is therefore considered to be a respiration product rather than an intermediate product in photosynthesis. J. K.

Influence of the Pyrrole Nucleus in the Formation of Chlorophyll. II. B. ODDO and G. POLLACCI (*Gazzetta*, 1920, **50**, i, 54—70. Compare A., 1915, i, 1083).—Previous publications on this subject having been discussed, the preparation of magnesium pyrrole-2-carboxylate, and experiments on the influence of nutrient solutions containing this compound on the growth of various plants, are described.

Magnesium pyrrole-2-carboxylate, $\left[\begin{matrix}CH{-}CH\\ \| \\ CH{\cdot}NH\end{matrix}\!>\!C{\cdot}CO_2\right]_2 Mg,2H_2O$, obtained by heating an aqueous-alcoholic solution of pyrrole-2-carboxylic acid (2 mols.) with magnesium oxide (1 mol.), crystallises in brush-like aggregates of needles or stellar aggregates of leaflets, and begins to decompose at about 260°.

The culture experiments were made with *Zea maïs*, *Solanum nigrum*, *Datura stramonium*, *Euphorbia* sp., and *Aster sinensis*, the culture liquids containing calcium nitrate, ammonium sulphate, potassium nitrate, and potassium dihydrogen phosphate (or magnesium pyrrole-2-carboxylate), all carefully purified from traces of iron. The results show that, in the nutrient solutions containing the pyrrole compound, the plants exhibit normal growth, whereas in those free from this compound, plants are obtained with leaves showing marked chlorosis.

Thus, plants grown in a nutritive medium containing an assimilable pyrrole derivative form chlorophyll, even in absence of iron. When no such pyrrole derivative is present, iron constitutes an indispensable element in order that the plastids may become green, and acts, indeed, as a catalyst in the formation of the pyrrole nucleus, which constitutes the centre of the whole chlorophyll complex. Pyrrole and magnesium are, then, the substances which cause plants to become green. T. H. P.

Influence of certain Organic Compounds on the Development of Plants. IV. G. Ciamician and C. Ravenna (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 7—13. Compare A., 1919, i, 241).—Further experiments have been made with bean plants watered with 0·1% solutions of various compounds. Of the normal amines, methylamine is the least toxic, whilst the toxicity diminishes continuously in passing from ethylamine to *n*-amylamine; the action is manifested by the appearance of yellow, translucent spots on the leaves, the plants being killed by ethylamine and rendered less vigorous by the other amines. *iso*Amylamine is somewhat more poisonous than *n*-amylamine, and determines a characteristic albinism of the compound leaves, which are deprived of chlorophyll either entirely or everywhere but along the principal veins; this albinism recalls that due to nicotine, which is accompanied by *iso*amylamine in tobacco. Potassium *n*-butyrate is without apparent effect, whereas the *iso*butyrate causes partial falling of the leaves.

Formamide causes fall of the seed-leaves, probably owing to the presence of the aldehydic group, whilst acetamide is completely innocuous. Oxalic acid causes less vigorous growth than succinic acid. Methyl and, especially, ethyl tartrates produce on the seed-leaves translucent spots, which lead to slow desiccation of the plants. Pyridine allows the plants to develop normally, but picoline produces yellow spots on both the seed-leaves and the compound leaves, without, however, injuring the plants seriously. The influence of the introduction of methyl groups into a molecule

is exhibited more markedly with derivatives of piperidine, which itself is only slightly toxic, whereas 1-methylpiperidine and coniine are highly toxic. Quinoline, *iso*quinoline, and 2-methylquinoline are all intensely toxic, the last more so than the first two, the effects of which are equal. Cocaine kills the plants, ecgonine and the methyl ether of norecgonine produce brown spots on the seed-leaves, but do not prevent further development, although with the former this is restricted; norecgonine produces no apparent effect. Unlike tetramethylammonium salts, betaine is only slightly toxic, producing merely partial withering of the seed-leaves.

With broad bean, pumpkin, and tomato plants, less marked effects are obtained than with beans, but those substances which act most intensely on the latter affect these three plants similarly.

Certain substances, especially morphine and catechol, give an exceptionally dark green colour to the leaves, but the absorption spectra of alcoholic extracts of such leaves exhibit no qualitative difference, but only a different intensity of absorption from those obtained with normal leaves; photometric measurements indicate the presence of twice as much chlorophyll in the former as in the latter leaves, but the proportion of starch present is no greater. Thus the quantity of starch present is not related to the intensity of the green colour of the leaves, and although most of the toxic substances examined favour the deepening of the colour, some, such as theobromine, produce the opposite effect.

The toxic substances investigated do not merely act on the roots, but pass into the tissues of the plant. With catechol, however, no trace is detectable in the plant, this compound being probably destroyed by enzymic action (compare A., 1918, i, 93).

T. H. P.

The Lipolytic Activity of the Castor and Soja Bean. ARTHUR WILLIS BARTON (*J. Amer. Chem. Soc.*, 1920, **42**, 620—632).—Preliminary to a study of the activity of the lipases of castor and soja beans, it was shown that Falk's method of determining the liberated fatty acids (A., 1912, i, 522) is inapplicable when lard or olive oil is used as a substrate; complete neutralisation is only achieved by the addition of alcohol and ether to produce a homogeneous solution before titration with aqueous alkali hydroxide. In the case of castor beans, the husks were removed for the preparation of the lipase, because its activity was in this way doubled, but this was unnecessary with soja beans. From his results the author deduces that (1) castor bean lipase is more intense in its action than soja bean; (2) the ranges of acidity of medium in which action on lard and olive oil takes place are practically the same for the two lipases (0·0—0·5% hydrochloric acid), and are independent of the substrate; (3) the degree of activity for a given acidity is practically the same for olive oil and for lard, the maximum for castor bean being at 0·2% and for soja bean at 0·4%; (4) the activity towards ethyl butyrate is less, and the range of acidity in which

action takes place is much higher and shorter. It is concluded th soja and castor beans contain more than one, but the same, lipases
J. K.

Proso Millet—Analysis of the Oil—a Characterist Alcohol. B. A. DUNBAR and E. R. BINNEWIES (*J. Amer. Che Soc.*, 1920, **42**, 658—666).—The oil extracted from proso mille *Panicum miliaceum*, by ether or light petroleum gradually deposi thin, pearly-white plates, m. p. 279° (corr.), soluble in most orga solvents, but sparingly in cold ether or alcohol. As it could not identified, it was called "*prosol*." It has the formula $C_{24}H_{36}O_2$, ca be acetylated, and with hydroxylamine gives an unsatisfactor quantity of a precipitate, presumably an oxime. The formation c a fluorescein, under conditions vaguely specified, is looked on as ev dence of a ring structure, with two side-chains in the ortho-positio The oil itself is a semi-drying oil, comparable with rape-seed oi [For analytical details, see *J. Soc. Chem. Ind.*, 1920, .]
J. K.

Chemical Examination of the Root of Nerium Odorun (Kanher). SHUNKER TRIMBAK GADRE (*J. Ind. Inst. Sci.*, 1916, 1 181—199).—The air-dried roots of *Nerium Odorum* collected i winter in the Krishna valley, when extracted with hot alcohol, los 13·7% of their weight. The alcoholic extract, when distilled i steam, yielded a small amount of an orange-coloured essential oi having D_4^{30} 0·8660; $[\alpha]_D^{31}$ −4·088°; n_D 1·40315. Of the total residua extract, 45% was soluble in water, and this aqueous solution con tained a small amount of a crystalline phenolic compound, m. p 140—141°, a considerable amount of a glucoside, and free dextrose The portion of the extract insoluble in water, constituting 7·5% o the original root, was composed of a hard and a soft resin. Fron the hard resin the author isolated formic and butyric acids in traces oleic, linolic, palmitic and stearic acids, a new alcohol, *kanerol* $C_{30}H_{50}O$, m. p. 185·7—186·2° (corr.), $[\alpha]_D^{30}$ +80·1°, giving an *acety* derivative, m. p. 208—210°, $[\alpha]_D^{30}$ +84·88°, and a *benzoyl* deriv ative, m. p. 189—190°. In addition, the hard resin contained small quantity of an aromatic acid, m. p. 243—245°. The soft resi contained oleic, linolic, palmitic and stearic acids, and the alcoho kanerol, which gave the colour reactions for a phytosterol, and i most respects closely resembled α-amyrin.

The ethyl acetate and the alcohol extracts of the hard resin wer found to consist mainly of resin acids.
W. G.

Okra Seed Oil. GEORGE S. JAMIESON and WALTER F. BAUGHMA (*J. Amer. Chem. Soc.*, 1920, **42**, 166—170).—The chemica characteristics of four samples of the cold-pressed oil from okr seed (*Abelmoschus esculentus*, Malvaceæ) have been determined These oils vary somewhat in composition. A recently expresse oil contained the glycerides of palmitic acid (27·23%), stearic aci (2·75%), arachidic acid (0·05%), oleic acid (43·74%), linolic aci

Pimpernel Saponin. CONRAD VESTLIN (*Pharm. Zentr.-h.*, 1920, **61**, 77—78).—Roots of *Pimpinella saxifraga germ.* yielded 1·107% of a saponin having the formula $C_{23}H_{36}O_{18},2H_2O$.

W. P. S.

Hydrocyanic Acid Content of Phaseolus lunatus. II. H. LÜHRIG (*Chem. Zeit.*, 1920, **44**, 262. Compare this vol., i. 359).—Further experiments on hydrocyanic acid in *Phaseolus lunatus* beans showed that treatment of the beans with saliva did not increase the amount of hydrocyanic acid above that formed by the action of the natural enzyme of the beans; prolonged action of saliva tended to reduce the amount of hydrocyanic acid. The residues remaining after the removal of the hydrocyanic acid by distillation were treated with emulsin, saliva, bile, and pancreatic juice, but no further amount of hydrocyanic acid was obtained.

W. P. S.

Urease of the Seeds of Robinia pseudacacia. P. Y. YI (*Ber. deuts. pharm. Ges.*, 1920, **30**, 178—191).—The quantity of ammonia liberated in the enzymic decomposition of urea by the powdered seeds of *Robinia pseudacacia* increases proportionately with the amount of seed powder used and the duration of the action, and the decomposition is accelerated by raising the temperature to 37°. The most active preparations of the urease are obtained by precipitation with alcohol from an aqueous extract of the seeds, although this causes some injury to the enzyme. Lead acetate, sodium chloride, and ammonium sulphate are still less suitable precipitants. When salt solutions of equal concentration are used, the most energetic action on urea is obtained with sodium acetate solution. Pure water dissolves most urease at 40°, the activity of the aqueous solutions decreasing with the rise in temperature, and practically ceasing at 80°. The fact that the urease of *Robinia* seeds is only partly soluble in water supports the view that two or more ureases differing in physical properties are present. *Robinia* urease decomposes *as*-dimethyl- and diethyl-carbamides, but has little, if any, action on the corresponding symmetrical compounds.

C. A. M.

The Hydrocyanic Acid Question. IV. The Seeds of Schleichera trijuga. L. ROSENTHALER (*Schweiz. Apoth. Zeit.*, 1920, **58**, 17—20; from *Chem. Zentr.*, 1920, i. 338. Compare this vol., i. 130).—Uncombined hydrocyanic acid is not present in the seeds of *Schleichera trijuga*, Willd.; a compound of it, however, can be removed from the oil with ether or light petroleum, which is not identical with amygdalin, phaseolunatin, or linamarin. It does not appear to be a glucoside, but is possibly a hydroxynitrile.

H. W.

The Function of Vitamines in the Metabolism of Sclerotinia cinerea. J. J. WILLAMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 549—585).—The solutions found by Currie (A., 1917, i, 614) to promote the growth of *Aspergillus niger* failed when

applied to the case of *Sclerotinia cinerea* (Bon.), Schröter, the brown rot organism of peaches and plums, but normal development took place when small amounts of peach, prune, or apple juice were added, that of the first being most effective. A variety of nitrogen compounds, sugars, pectin, and salts of organic and inorganic acids were also ineffective when not contaminated with mother liquors from a plant juice. It is therefore suggested that the vitamines present in the juices are responsible for their influence.

By means of adsorption with fuller's earth, vitamine preparations were made from many and most varied sources, both plant and animal. All these preparations were active in promoting growth of *Sclerotinia*; a few of them also promoted reproduction.

Some experimental evidence was obtained favouring the view that there might be two separate vitamine factors involved in the two phases, vegetation and reproduction, but, on the other hand, the hypothesis of but a single vitamine for *Sclerotinia* is more plausible and accords with much of the experimental evidence, and it is very probable that reproduction in *Sclerotinia* is simply a different manifestation of the same activities as characterise vegetation. The *Sclerotinia* vitamine is possibly identical with water-soluble *B* of the higher animals. J. K.

Composition of Hubbard Squash Seed Oil. WALTER F. BAUGHMAN and GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1920, **42**, 152—157).—The seeds of *Cucurbita maxima* contained 5·72% of moisture and 36·66% of matter soluble in ether. The cold, pressed oil had D_{25}^{25} 0·9179, n^{25} 1·4714, iodine number (Hanus) 121·0, saponification number 191·5, Reichert-Messel number 0·37, Polenske number 0·39, acetyl number 27·8, acid number 0·50. Chemical examination showed the presence of the glycerides of palmitic acid (13%), stearic acid (6%), arachidic acid (trace, about 0·04%), oleic acid (37%), and linolic acid (44%). The unsaponifiable matter amounted to 1%. H. W.

Nicotine in Tobacco: Genesis and Function of Alkaloids. LUIGI BERNARDINI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 62—66).—The results of the author's experiments are as follows. Nicotine is not present in the seed of the tobacco plant, and is harmful to its germination, as also are larger doses of other compounds which contain heterocyclic nuclei and are related chemically to nicotine, such as pyridine and picoline. The alkaloid appears in the young plant immediately the chlorophyll begins to function, and originates in the leaves. The plant, which in its normal development contains the nicotine in its elaborating organs in virtue of the greater vital activity there developed, responds to any serious traumatic lesion, such as cutting, which attacks it at an important stage of its vegetative cycle, the alkaloid being thereby produced in increased quantity and localised in the regions adjacent to the lesion. The localised nicotine of the roots, and especially that accumulated in the leaves, is not utilised by the

lant even when the latter is placed in conditions favourable to uch utilisation.

These results lead to the assumption that the nicotine, probably ormed from certain residues of the nitrogen katabolism, is laborated by the plant in order either to prevent accumulation of uch residues in the organism or to utilise them, with intensification of their harmfulness, in defence of its organs. An analogous ase is that of tannin, which is elaborated by plants to prevent ccumulation of polyhydric phenolic residues; the tannin is erhaps more injurious than these residues, but it may be utilised y the plant, being localised, by a simple mechanism, in the wood or its formation and preservation. T. H. P.

Urea and other Sources of Nitrogen for Green Plants. BOKORNY (*Pflüger's Archiv*, 1918, **172**, 466—496; from *Physiol. bstr.*, **4**, 57).—Green plants are capable of disintegrating and tilising almost as many organic substances as the fungi are. Urea n an initial concentration of 0·05% has a beneficial action on the rmination of wheat, and acts as nutrient to the seedlings. 0·1% as a harmful action. J. C. D.

Effect of Lime on the Sodium Chloride Tolerance of Wheat Seedlings. J. A. LECLERC and J. F. BREAZEALE (*J. Agric. es.*, 1920, **18**, 347—356).—As a result of water culture and sand ilture trials with wheat seedlings, it is shown that very small nounts of calcium oxide or sulphate overcome the toxic effects of dium chloride or sulphate. Magnesium sulphate and barium iloride are slightly antagonistic to sodium chloride, but potassium iloride, sodium nitrate, sodium phosphate, ferric chloride, and um have no effect on the toxicity of sodium chloride.

Under the experimental conditions, the presence of lime did not event the entry of sodium chloride or sulphate into the plant, e antagonistic effect of lime not being due, apparently, to its fect on the permeability of the cells, but to some other cause.

The higher tolerance to alkali salts shown by plants in soil or nd cultures as compared with those grown in water cultures is ot due entirely to the physical effects of the presence of solid rticles of different degrees of fineness, but also to certain soluble bstances which are sometimes present in very small quantities. W. G.

Enzymes. III. Invertase and other Enzymes of Germinated Barley. D. MAESTRINI (*Atti R. Accad. Lincei*, 1919, [v], 3, ii, 509—511. Compare this vol., i, 273).—Germinated barley ied at temperatures below 40° contains invertase, extractable 0·003 mol. % acetic acid solution, and present, not only in the nulsion, but also in the filtrate of the extract; the enzyme acts st at about 50°, and is destroyed at 55°. The extract of the rminated barley contains no maltase, lactase, or rennase, the agulation of milk produced by the extract being due solely to e acidity of the latter, as it is effected even by the boiled extract. catalase and an oxydase are, however, present in the germinated rley. T. H. P.

Constituents of Protein in Polished Rice. JUNZO KUROSAWA (*J. Tokyo Chem. Soc.*, 1919, **40**, 551—561).—In connexion with the nutritive value of various proteins, the nature of the rice protein has been reinvestigated. Dry, pure, polished rice contains 1·77% of total nitrogen, 1·14% of protein nitrogen, 0·13% of non-protein nitrogen, and 7·125% of total protein (=protein nitrogen × 6·25). The protein nitrogen contains 97·82% soluble in hot hydrochloric acid, 97·81% soluble in hot 30% sulphuric acid, 3·58% of humin (I) nitrogen, 9·20% of ammonia nitrogen in sulphuric acid, 1·18% of humin (II) nitrogen, 20·40% of nitrogen precipitated by acid, and 63·12% of other nitrogen in sulphuric acid. Of the total nitrogen, 10·89% is attributable to arginine, 8·89% to histidine, and 2·67% to cystine; these amounts are quite different from those recorded by other investigators. Cystine corresponds with 0·87%, tyrosine with 3·51%, and tryptophan with 0·88%, calculated on the dry material.

Matsui's observation is confirmed that guanidine nitrogen is eliminated in the Van Slyke method if the reaction is allowed to proceed for several hours. CHEMICAL ABSTRACTS.

Enzyme Action. XVIII. The Saccharogenic Actions of Potato Juice. GRACE McGUIRE and K. GEORGE FALK (*J. Gen. Physiol.*, 1920, **2**, 215—227. Compare A., 1919, i, 426).—The marked action of the juice alone and also in the presence of added starch at p_H 4 to 5 is due to the hydrolysis of sucrose or raffinose by the sucrase present. There is very little degradation of starch. At p_H 6 there is action both on the part of the sucrase and the amylase, whilst at p_H 7 to 8 the action of the amylase is alone observable. J. C. D.

Nutritive Factors in Plant Tissues. III. Further Observations on the Distribution of the Water-soluble Vitamine. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with the co-operation of ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1920, **41**, 451—468).—An attempt to place our knowledge of the value of certain foodstuffs as sources of the accessory factors on a quantitative basis. Lucerne and clover are extraordinarily rich in water-soluble *B*. Of the ordinary vegetables, tomatoes appear to be richest, whilst spinach, cabbage, turnip, and carrot are not quite so potent. The beetroot is not equal in this respect to the other roots tested, and Timothy hay also proved disappointing. The potato is evidently rich in the water-soluble *B* factor, which does not appear to be concentrated to any extent in the surface layers. No differences were noted in the food value of old and new potatoes. J. C. D.

Salt and Alkaline Soils. Origin of Sodium Carbonate in Soils. A. DE DOMINICIS (*Staz. sperim. agrar. Ital.*, **51**, 103—161 from *Chem. Zentr.*, 1918, ii, 982—983).—In considering the problem of irrigation of southern soils, account must be taken of

the relationship between irrigation, movement, distribution, and transformation of the neutral sodium salts. Incautious irrigation frequently defeats its purpose, since it results in raising the subterranean salt water, concentration of the salts in the surface layers, and formation of sodium carbonate instead of neutral salts; the occurrence of the carbonate renders the soil less fit for cultivation than does that of neutral salts. The carbonate can be removed by simple washing with water, but this involves the loss of all colloidal mineral and organic substances. Double decomposition between sodium chloride or sulphate and calcium carbonate plays little, if any, part in the production of sodium carbonate. This is shown by the fact that the presence of sodium chloride and sulphate hinders the formation of the carbonate, the latter only appearing after removal of the neutral salts, and being formed to a greater extent in proportion as the removal is more thorough. Nevertheless, an alkaline soil is indirectly dependent on a salt soil. The phenomenon is explained by Gedroiz on the assumption that sodium chloride and sulphate form peculiar compounds in the soil, which can only enter into reaction after removal of the salts to which they owe their origin. These are regarded as absorption compounds, and as being formed by double decomposition between absorbed substances, such as compounds of calcium and magnesium and sodium chloride and sulphate. The extent of the formation of sodium carbonate depends on the intensity and length of action of the neutral salts and on the content of adsorbed sodium which can be extracted with 10% hydrochloric acid.

The author's experiments lead him to a quite different conception of the action. The alkalinity depends primarily on absorbed sodium, but results from the hydrolysis of the "absorbates" when they leave the state of coagulation; the sodium hydroxide so formed can then react with calcium carbonate, but, more commonly, is converted into sodium carbonate by carbon dioxide. Actually, an alkaline reaction can be observed in the absence of calcium carbonate and carbon dioxide. The part played by the neutral salts consists in holding the absorbates in a coagulated condition, in which they are not hydrolysed. The action of gypsum in improving an alkaline soil does not consist in simple neutralisation of sodium carbonate. The carbonate and bicarbonate derived from it, together with the excess of gypsum, coagulate the colloids and change them again into calcium adsorbates, the action being facilitated by the presence of neutral sodium salts. The latter can themselves act helpfully in the removal of alkalinity, but only indirectly and in virtue of the corresponding anions. The prescribed irrigation with salt water is dangerous for the soil, since it inhibits the formation of sodium absorbates; the danger could, however, be avoided by simultaneous treatment with gypsum.

Organic compounds play a part in the formation of sodium carbonate in the soil. Among colloidal mineral substances, those of zeolitic nature, which by double decomposition can yield absorbents, are active; of these, the chabasite type, corresponding with

aluminium silicate, is the most important, whilst substitution occı very slowly and dissociation takes place with greater difficulty wi substances of the natrolitic type. H. W.

Absorption of Lime by Soils. F. J. WARTH and MAU PO SAW (*Mem. Dept. Agric. India*, 1919, **5**, 157—172).—A stu of the absorption by different types of soils of calcium carbona from solutions of calcium hydrogen carbonate at different conce trations and in the presence of varying amounts of carbon dioxid On the results, a method for estimating the lime requirements a soil is based and described. W. G.

The Action of Lime in the Soil. JOHN HUGHES (*J. Ba & W. & S. Co. Soc.*, 1919, [v], **13**, reprint, 10 pp.).—A study the rate of carbonation of calcium oxide when mixed with fo times its weight of soil (*a*) in the air-dry state, (*b*) kept moist wi water and placed outdoors. Two types of soil were used, one co taining 3·85% and the other 14·97% of organic matter and con bined water. In both soils, which were exposed to the air in moist state, the whole of the calcium oxide was carbonated with six weeks. The author discusses the results of Voelcker's exper ments carried out at Woburn on the lime–magnesia ratio in soil The lime and magnesia contents of eleven Herefordshire soils a given, and in all cases where the magnesia was in excess of tl lime, full-crop results were not obtained. W. G.

The Relation of certain Acidic to Basic Constituen of the Soil affected by Ammonium Sulphate and Sodiu Nitrate. L. P. HOWARD (*Soil Sci.*, 1919, **8**, 313—321).- The soils used were from permanent experimental plots which f the last twenty-five years have received, respectively, ammoniu sulphate and sodium nitrate, half of each plot being limed. A exchange of bases, produced by treatment of the soil with a sol tion of potassium chloride, showed a marked degree of reser acidity from the unlimed soil receiving ammonium sulphate. Th acidity, so developed, showed a correlation with the acidity of a aluminium salt equivalent in amount to the weight of aluminiu found in the extract. Digestion with hydrochloric acid showe that the quotient obtained by dividing the sum of the weights the oxides of aluminium and iron by the sum of the weights the oxides of calcium and magnesium ranged from 85 in the ca of the unlimed soil receiving ammonium sulphate to 10 where lin and sodium nitrate were applied. Thus in these acid unlime soils, iron and aluminium partly took the places occupied b calcium and magnesium in the limed soils. The soil solution ac as a buffer solution containing phosphates and carbonates, and tl hydrogen-ion concentration in the soil solution from the unlime plot receiving ammonium sulphate was very similar to that pr duced by the addition of even quite large amounts of aluminiu salts to buffer solutions. W. G.

Organic Chemistry.

The Chemical Mechanism of Organic Rearrangements. ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1920, **42**, 787—821).—A theoretical paper dealing with rearrangement as determined by the affinity, energy, and spatial relationships of the atoms involved. Intramolecular rearrangements are determined by the free chemical energy at the interchanging atoms or groups, their affinity for each other and for the atoms in the groups to which they migrate, the amount of energy required to separate the migrating portion from the remaining atoms of the group, and the heats of formation of the isomerides or the two products. In a heterogeneous chemical system, change in chemical structure of a compound may be due to catalytic influence or to chemical action of the energy in the reagent employed, involving loss of a component part of the compound and subsequent isomerisation of the residual structure. A polymolecule may be produced by union of the compound with the reagent, when, owing to the chemical energy so added, isomerisation in the compound portion of the product takes place, resulting in partial conversion of its free energy into bound energy and heat, and subsequent decomposition of the system into the isomerised product and the reagent. These considerations are applied to critical reviews, which do not lend themselves to abstraction, of the various hypotheses proposed in explanation of the Hofmann conversion of bromoamides into primary amines, the rearrangements of aliphatic and aromatic $\alpha\beta$-glycols under the influence of acid, the pinacolin change, the rearrangements of aryl iodohydrins, and the formation of benzilic acid from benzil. A general consideration is also given of the production of intermediate products in such reactions. In regard to the question as to whether elimination of groups of atoms, for example, hydrogen and bromine from ethyl bromide, takes place from the same carbon atom or from more than one, it is concluded that, generally speaking, the former is of rare occurrence, because the latter usually results in a greater increase in entropy. J. K.

Oxidative Decomposition of Hydrocarbons. H. HEINRICH FRANCK (*Chem. Zeit.*, 1920, **44**, 309—310).—Aliphatic hydrocarbons of high molecular weight, such as paraffin oils and waxes, are oxidised to carboxylic acids and other oxidation products when decomposed by heat in the presence of oxygen and a catalyst. By varying the conditions of the oxidation, different proportions of volatile and non-volatile fatty acids may be obtained. Good results are obtained by the use of compounds of lead, mercury, manganese, vanadium, and chromium as catalysts, whilst alkalis and alkaline earths may also be used. In practice, good yields of fatty acids, ranging from acetic to arachidic acid, may be obtained by heating

paraffin wax in an autoclave at 150° in the presence of oxygen and 0·5 to 5% of catalyst, although eventually the oxidation may also be effected without a catalyst. The resulting fatty acids were separated by converting them into esters, which were fractionally distilled. The product obtained from an expressed paraffin-wax residue yielded 57·1% of fatty acids of lower molecular weight and 40·7% of acids of higher molecular weight, and contained unsaponifiable matter, from which a ketone melting at 46—50°, probably a mixture of stearone with other ketones, was separated. An edible fat resembling coconut oil was prepared by esterifying the mixed fatty acids thus obtained with ethylene glycol and 3% of sulphuric acid. [See, further, *J. Soc. Chem. Ind.*, 1920, 395A.]

C. A. M.

Brodie's Myricyl Alcohol. ALBERT GASCARD (*Compt. rend.*, 1920, **170**, 886—888).—Brodie attributed to the myricyl alcohol obtained from beeswax the formula $C_{30}H_{61}\cdot OH$. The author has prepared this alcohol and the corresponding iodide, and from careful analyses of the latter, and by preparation of the corresponding saturated hydrocarbon and comparison of the properties of the alcohol and its derivatives with known compounds in a near position in the same series, he concludes that myricyl alcohol has the formula $C_{31}H_{63}\cdot OH$. Finally, from lacceric [dotriacontanoic] acid, $C_{32}H_{65}\cdot CO_2H$ (A., 1914, i, 1045), he has prepared myricyl alcohol by degradation, and from myricyl alcohol, by conversion into the cyanide and hydrolysis, obtained lacceroic acid.

W. G.

The Equation of State of Ethyl Ether. E. ARIÈS. (*Compt. rend.*, 1920, **170**, 871—875).—By the use of equations already established, the author has calculated the saturated vapour pressures and the differences of the molecular volumes of the saturated fluid for ethyl ether for each 10° from −10° to 190°, and his results are in fairly close agreement with those obtained by Young. Finally, he finds for the heat of vaporisation of ethyl ether at 30° the value 85·63 cal., the value given by Young being 85·18 cal. W. G.

The Decomposition of Nitric Esters by Lime. THOMAS MARTIN LOWRY, KENDALL COLIN BROWNING, and JOSHUA WILLIAM FARMERY (T., 1920, **117**, 552—561).

Action of the Normal Methyl and Ethyl Sulphates on the Alkali Phosphates in Aqueous Solution. OCTAVE BAILLY (*Compt. rend.*, 1920, **170**, 1061—1064).—Methyl sulphate reacts with an aqueous solution of trisodium phosphate to give 77·8% of disodium methyl phosphate and 6·2% of sodium dimethyl phosphate, the former being converted into its barium salt, which may readily be isolated. With ethyl sulphate, the yield of the monoethyl phosphate is much lower and of the diethyl phosphate slightly higher. If disodium hydrogen phosphate is used in place of the trisodium salt, the total yield of the esters is lower, and sodium

lihydrogen phosphate or phosphoric acid does not react in aqueous olution with methyl or ethyl sulphate. W. G.

The Constitution of the Glycerophosphoric Acids. OCTAVE BAILLY (*Bull. Soc. chim. biol.*, 1919, **1**, 152—162).—By decomposition of barium glycerophosphate, obtained from lecithin, with odium carbonate in aqueous solution, a solution of sodium glycerophosphate was obtained, which was separated into two fractions, one crystalline and the other non-crystalline.

The non-crystalline fraction gave a calcium salt, which yielded on oxidation with bromine water evidence of the formation of an ther of dihydroxyacetone. This points to the calcium salt being a salt of α-glycerophosphoric acid. The crystalline sodium salt ppears to be a derivative of the β-acid. Therefore the glycerophosphoric acid obtained by the hydrolysis of lecithin is a mixture of the two isomerides. J. C. D.

Action of Water on ββ′-Dichlorodiethyl Sulphide. CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1920, **170**, 845—848).—ββ′-Dichlorodiethyl sulphide is slowly decomposed by cold water nd rapidly by boiling water, giving hydrochloric acid and dihydroxydiethyl sulphide. The reaction is an equilibrium phenomenon, nd is considerably influenced by the temperature and the relative proportions of dichlorodiethyl sulphide and water used. Both acids and alkalis exert a retarding influence on the decomposition.

The solubility of dichlorodiethyl sulphide in cold water is 0·48 gram per litre. It is increased by the presence of dihydroxydiethyl sulphide. The presence of the latter in small amounts also accelerates the decomposition of dichlorodiethyl sulphide, but as its concentration increases, the velocity of decomposition decreases.
W. G.

Sulphur Derivatives of Butyl Alcohol. H. LEB. GRAY and GURNEY O. GUTEKUNST (*J. Amer. Chem. Soc.*, 1920, **42**, 856—860).—Dibutyl sulphide is best prepared by boiling aqueous olutions of sodium butyl sulphate and sodium sulphide in a reflux pparatus, and subsequently distilling; if the mixture is distilled without previous boiling, butyl mercaptan is also produced. The method of oxidation of the sulphide to the sulphone by nitric acid, recommended by Grabowsky (1874), is untrustworthy, but excellent esults are obtained by the use of sodium permanganate in neutral olution. J. K.

Catalytic Decomposition of Fatty Acids by Carbon. J. B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1920, **170**, 1064—1067).—When acetic acid or its homologues are passed over purified animal charcoal at 360—380°, the acids are decomposed, giving a mixture of carbon dioxide, ethylenic hydrocarbons, carbon monoxide, methane and its homologues, and hydrogen, together with water and small amounts of ketones and aldehydes. With carbon from sugar, a considerably higher temperature is necessary, but the products are much the same. W. G.

Remarkable Similarity in the Form of Crystals and Microbes. ARMINIUS BAU (*Zeitsch. techn. Biol.*, 1919, **7**, 203—213; from *Chem. Zentr.*, 1920, i, 495).—With the aid of microphotographs (magnification, 1000 times), the author describes crystals of calcium oxalate which differ from the usual crystals in such a manner that they can easily be mistaken for *Saccharomycetes* or rod-like bacteria. The crystals are obtained by precipitation of solutions containing oxalic acid with calcium acetate, and may readily be distinguished from living matter by their ready solubility in moderately dilute hydrochloric, nitric, or sulphuric acid.

H. W.

Preparation of Fat and Wax-like Substances. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 318222; from *Chem. Zentr.*, 1920, ii, 536).—Adipic acid or its derivatives or homologues is esterified with dihydroxylated hydrocarbons or their derivatives. *Glycyl adipate* is obtained as a tallow-like mass when adipyl chloride dissolved in pinacolin is treated with a solution of ethylene glycol and pyridine in the same solvent; the ester may also be prepared from ethylene dibromide and potassium adipate. *Glycyl α-methyladipate*, brown, waxy mass, is obtained from ethylene oxide and α-methyladipic acid. *Propyleneglycyl adipate*, from propylene iodide and potassium adipate, resembles butter.

H. W.

The Supposed Methanetetracarboxylic Acid. EYVIND BŒDTKER (*Bull. Soc. chim.*, 1920, [iv], **27**, 257—258).—The substance previously described as methanetetracarboxylic acid (compare A., 1916, i, 2) is now shown to be ammonium tetraoxalate.

W. G.

Preparation of Glyoxal. ALEXANDER BOSSHARD (Brit. Pat. 140478).—When ozone acts on acetylene in presence of a large proportion of air, oxygen, or other indifferent gas, the reaction ceases to be violent in character and results in the production of glyoxal. Proportions which have been found successful are 1—2% of ozone, 3—4% of acetylene, and 94—96% of air. The process is facilitated by the presence of water vapour or the use of a water spray, whereby the glyoxal is washed out of the gaseous mixture and separates as a concentrated solution. G. F. M.

Experiments on the Preparation of Oximino-derivatives. WILLIAM KERSHAW SLATER (T., 1920, **117**, 587—591).

Glucal and its Conversion into New Substances of the Dextrose Series. EMIL FISCHER, MAX BERGMANN, and HERBERT SCHOTTE (*Ber.*, 1920, **53**, [*B*], 509—547).—A further study of glucal and its derivatives (A., 1913, i, 445; 1914, i, 252) leads the authors to assign the formula

$$OH\cdot CH_2\cdot CH(OH)\cdot \underbrace{CH\cdot CH(OH)\cdot CH{:}CH}_{O}$$

to the parent substance, for the following reasons. Glucal triacetate can be converted into *d*-glucosephenylosazone, thus showing that glucal contains the normal carbon chain present in dextrose, and also that a saturated carbon atom unattached to oxygen is not present. The transformation of glucal triacetate into *d*-arabinose by means of ozone proves the double bond to be between the first and second atoms of the carbon chain. The presence of the furan ring accounts for the colour reaction with a pine shaving and the observed individuality of one of the acetyl groups of glucal triacetate. Only three oxygen atoms of hydroglucal are present in hydroxyl groups, and the stability of the substance towards hydrochloric acid renders the presence of an ethylene or trimethylene oxide ring improbable. The location of the tetramethylene ring in the glucal molecule is deduced from the smooth conversion of glucal triacetate into a derivative of dextrose, and from the proof that the carbon atom, 6, does not participate in the formation of glucal.

Glucal triacetate is transformed by ozone in glacial acetic acid solution into *d*-arabinose triacetate and the *triacetyl* derivative of a pentanetetrolic acid (probably arabonic acid), long needles or prisms, m. p. 127° after much softening at 120°, $[\alpha]_D^{17} + 27.23°$ in alcoholic solution; the former showed little tendency to crystallise, and was therefore immediately hydrolysed to *d*-arabinose, which was identified as the p-*bromophenylhydrazone* and the *phenylbenzylhydrazone*, colourless, shining leaflets, m. p. 177—178° (corr.), $[\alpha]_D^{16} + 14.4°$ in methyl alcohol.

Glucal triacetate is converted into *d*-glucosephenylhydrazone by the following process. The additive product of bromine and glucal triacetate (Fischer, *loc. cit.*) is treated with silver acetate, and thus converted into a mixture of stereoisomeric *tetra-acetylglucose-β-bromohydrins*, OAc·CH_2·CH(OAc)·CH·CH(OAc)·CHBr·CH·OAc (the two CH groups linked through O),

which is deacetylated by dilute hydrochloric acid and then treated with phenylhydrazine; the yield is about 60%.

Glucal triacetate reacts with a saturated solution of hydrogen bromide in glacial acetic acid to yield *glucal diacetate hydrobromide*, slender needles, m. p. 99—100°; the substance exhibits mutarotation in acetylene tetrachloride, chloroform, or alcohol, but is recovered unchanged from its solutions. It contains a free hydroxyl group, since it is transformed by acetic anhydride in the presence of pyridine into *glucal triacetate hydrobromide*, prisms, m. p. 82—85°, $[\alpha]_D^{19} + 54.43°$ in tetrachloroethane, which does not show mutarotation. The constitution of these substances has not been definitely elucidated.

The addition of bromine to glucal triacetate yields a mixture of unstable dibromides, from which on some occasions it has been found possible to isolate a crystalline compound, $C_{12}H_{16}O_7Br_2$, m. p. 117—118° (corr.), which, however, was not optically homogeneous and the isolation of which could not be subsequently effected after loss of seeding material. The corresponding *dichloride* proved to be more stable, but in spite of homogeneous appearance and

constant, if slightly indefinite, m. p. (92—94°), *it was likewise not* optically uniform, and appeared to consist of a mixture of varying proportions of stereoisomerides; the most active preparation had $[\alpha]_D^{15}$ +199·7° *in tetrachloroethane solution.* The *dichloride* is transformed by silver acetate in glacial acetic acid solution into *glucosetetra-acetate-β-chlorohydrin*,

$$OAc\cdot CH_2\cdot CH(OAc)\cdot \underbrace{CH\cdot CH(OAc)\cdot CHCl\cdot CH}_{O}\cdot OAc,$$

monoclinic-sphenoidal crystals, $a : b : c = 0·7786 : 1 : 0·7030$, β = 117°53½′, m. p. 110—111°, $[\alpha]_D^{18}$ +51·1° in tetrachloroethane.

Crude glucal triacetate dibromide is converted by methyl alcohol and silver carbonate into a mixture of *triacetylmethylglucoside-β-bromohydrins*: (1) rhombic, bisphenoidal crystals,

$$a : b : c = 0·2602 : 1 : 0·2855,$$

m. p. 139° (corr.), $[\alpha]_D^{18}$ +50·2° in tetrachloroethane, and (2) monoclinic, sphenoidal crystals, $a : b : c = 2·7028 : 1 : 1·6237$, β = 99°52′, m. p. 115—116°, $[\alpha]_D^{16}$ −92·0° in tetrachloroethane. The acetyl compounds can be deacetylated by methyl-alcoholic ammonia, and yield the corresponding *methylglucoside-β-bromohydrins*: (1) m. p. 181—182° (slight decomp.), $[\alpha]_D^{14}$ +0·87° in aqueous solution, and (2) m. p. 182—183° (corr.; decomp.), $[\alpha]_D^{16}$ −63·8° in aqueous solution; the former does not reduce Fehling's solution and is stable towards *N*-hydrochloric acid, whereas the latter is readily attacked. *Triacetylmethylglucoside-β-chlorohydrin*, thin prisms, m. p. 150—151° (corr.), $[\alpha]_D^{18}$ +40·0° in tetrachloroethane, is very readily obtained from glucal triacetate dichloride, only one modification appearing to be formed. On deacetylation, it gives *methylglucoside-β-chlorohydrin*, slender needles, m. p. 164° after softening at about 159°, $[\alpha]_D^{18}$ −12·05° in aqueous solution.

Methyl epi*glucosamine*, $OMe\cdot C_6H_{10}O_4\cdot NH_2$, is obtained in the form of its salts by the action of hot aqueous ammonia on methylglucoside-β-bromohydrin (1) or methylglucoside-β-chlorohydrin; the *hydrobromide* crystallises in needles, m. p. about 215° (decomp.), $[\alpha]_D^{22}$ −123·8° in aqueous solution, whilst the *hydrochloride* decomposes at 210—211° and has $[\alpha]_D^{19}$ −146·6° in water. The glucoside is not attacked by emulsin or yeast extract. Methyl *epi*glucosamine could only be isolated as a syrup. *Tetra-acetylmethyl* epi*glucosamine* is, however, smoothly obtained when the above hydrochloride is treated with acetic anhydride and dry pyridine at the ordinary temperature; it forms rhombic-bisphenoidal crystals, $a : b : c = 0·4279 : 1 : 0·3906$, m. p. 188°, $[\alpha]_D^{18}$ −119·2° in chloroform, and does not appear to be identical with the tetra-acetylmethylglucosamine described by Hamlin.

Treatment of either form of methylglucoside-β-bromohydrin with sodium amalgam and water (the chlorohydrin, however, is only extremely slowly affected) leads to the formation of *β-deoxymethylglucoside*, $OMe\cdot \underbrace{CH\cdot CH_2\cdot CH(OH)\cdot CH}_{O}\cdot CH(OH)\cdot CH_2\cdot OH$, which, in the absence of seeding material, is best purified through the triacetyl derivative; the pure substance has m. p. 122—123° (corr.),

$[\alpha]_D^{17}$ −48·22° in aqueous solution. It does not reduce Fehling's solution, but is readily hydrolysed by $N/10$-hydrochloric acid, but not by yeast extract or emulsin. *Triacetyl-β-deoxymethylglucoside* forms rhombic-bisphenoidal crystals, $a:b:c = 0·4701:1:0·5636$, m. p. 96—97° after softening at 91°, $[\alpha]_D^{18}$ −30·31° in tetrachloroethane solution.

Glucal diacetate-ζ-bromohydrin,

$$CH_2Br\cdot CH(OAc)\cdot CH\cdot CH(OAc)\cdot CH\colon CH\ (?),$$
(with an O bridge linking the second CH and the terminal CH)

needles, m. p. 44—45°, $[\alpha]_D^{16}$ −43·03° in tetrachloroethane, is obtained by the reduction of acetyldibromoglucose with zinc dust and acetic acid. It reduces Fehling's solution, adds bromine in chloroform solution, and gives a green coloration with a pine shaving; it does not, however, restore the colour of a magenta-sulphurous acid solution. H. W.

A Cello*iso*biose. H. Ost and R. Prosiegel (*Zeitsch. angew. Chem.*, 1920, **33**, 100).—A new biose has been isolated from the product of the acetylation of cellulose in presence of considerable quantities of sulphuric acid, the reaction being allowed to proceed for some days at 30°, or for some weeks at 15—20°, until crystals of the known cellobiose octoacetate begin to separate. *Celloisobiose*, $C_{12}H_{22}O_{11}$, is easily soluble in water, sparingly so in alcohol, and forms fine needles, which melt indefinitely at 165—190° with evolution of gas; in aqueous solution, $[\alpha]_D$ +23°. It has a slightly sweet taste, and its reducing property is 99% of that of maltose. It is not hydrolysed by yeast, but readily yields dextrose when treated with hydrochloric acid. Whilst cellobiose showed signs of fermentation after five days (compare, however, Schliemann, *Diss.*, Hanover, 1910), cello*iso*biose gave no carbon dioxide. J. K.

The Viscosity of Solutions of Cellulose. I. William Howieson Gibson. II. William Howieson Gibson [with Leo Spencer and Robert McCall] (T., 1920, **117**, 479—493).

Digestive Hydrolyses by Mechanical Ionisation of the Water. J. E. Abelous and J. Aloy (*Compt. rend.*, 1920, **170**, 1012—1014. Compare A., 1919, i, 310).—Simple shaking or bubbling of air through an aqueous solution or suspension of starch, lactose, neutral fats, or fibrin produces a partial hydrolysis, the amount increasing with rise in temperature. The addition of boiled digestive juices, such as saliva in the case of starch, or gastric juice in the case of fibrin, considerably increases the hydrolysis, although the enzymes in these juices were destroyed by the preliminary boiling. W. G.

The Supposed Fission of Starch by Formaldehyde. M. Jacoby, W. von Kaufmann, A. Lewite, and H. Sallinger (*Ber.*, 1920, **53**, [*B*], 681—685).—A reply to Woker's recent criticisms (this vol., i, 10). The simple explanation of the supposed diastatic action of formaldehyde lies in the fact that the latter forms a loose additive compound with starch (which does not give a blue color-

ation with iodine), and also modifies the physical properties of the colloid; precipitation with alcohol, or with numerous electrolytes which behave similarly, yields unchanged starch, which under no conditions has suffered diastatic degradation. H. W.

Some Properties of Inulin and Changes in its Physical State. J. WOLFF and B. GESLIN (*Bull. Soc. chim. biol.*, 1920, **2**, 19—23).—The hydrolysis of inulin is considered. Inulin prepared from chicory or dahlias is more soluble in water than that from other sources after it has been precipitated by alcohol. It can be converted into the less soluble form by evaporating the solution. The change is reversible, and is not fully understood. J. C. D.

The Diastatic Hydrolysis of Inulin. H. COLIN (*Compt. rend.*, 1920, **170**, 1010—1012).—In the hydrolysis of inulin by inulase from different sources, there is no indication of the formation of any intermediate products between inulin and the reducing sugars. W. G.

Preparation of Organic Derivatives of Calcium Iodide. WALTER SPITZ (D.R.-P. 318343; from *Chem. Zentr.*, 1920, ii, 601). —Aqueous or alcoholic solutions of calcium iodide are allowed to react with neutral aqueous or alcoholic solutions of organic derivatives of ammonia, such as free or combined amino-acids or carbamides, and the additive compounds are obtained in the solid state by evaporation or spontaneous crystallisation of the solutions. *Glycine calcium iodide*, $CaI_2,NH_2\cdot CH_2\cdot CO_2H,2H_2O$, crystallises from aqueous solutions of the components in colourless, prismatic needles which decompose, without melting, above 275°; the iodine is not completely precipitated by silver nitrate in nitric acid solution. *Carbamide calcium iodide*, $CaI_2,CO(NH_2)_2,2H_2O$, obtained by boiling an aqueous solution of the components with a few drops of acetic acid under reflux, forms large, transparent plates, m. p. 167·5°; the calcium is quantitatively precipitated by ammoniacal ammonium oxalate. *Glycylglycine calcium iodide*,

$$CaI_2,(C_4H_8O_2N_2)_2,2H_2O,$$

colourless needles, decomposes with separation of iodine, but without melting, above 200°. *Alanine calcium iodide*,

$$CaI_2,(C_3H_7O_2N)_2,2H_2O,$$

has m. p. 115°. The compounds are stable in air, not hygroscopic, and applicable in pharmacy; in contrast to calcium iodide, they are not decomposed by carbon dioxide. H. W.

Action of Chlorine, of Hypochlorous Acid, and of Cyanogen Chloride on Cyanamide and its Derivatives. CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1920, **170**, 998—1001).—When chlorine is passed over cyanamide, a yellow, highly polymerised product is obtained. When the gas is passed into an aqueous solution of the amide or of calcium cyanamide, a lachrymatory product is obtained. If the solution is then warmed, a red vapour is given off, which condenses below 0° to a red, extremely unstable liquid,

which explodes after a few minutes. When an aqueous solution of cyanamide is added gradually to an aqueous solution of hypochlorous acid free from chlorine, and the mixture cooled to 0°, a very unstable, crystalline product, dangerous to handle, is obtained. When perfectly dry silver cyanamide is added to an excess of cyanogen chloride at 0°, a white powder is formed, which is a *silver* compound, $AgN(CN)_2$, and swells up when heated. This silver compound is decomposed by hydrogen chloride in ethereal solution, giving *dicyanimide hydrochloride*, $NH(CN)_2,HCl$, which in its turn is decomposed by water to give biuret. If the silver compound, $AgN(CN)_2$, is decomposed in water by dilute hydrochloric acid, it gives *cyanocarbamide*, CN·NH·CO·NH_2. W. G.

Carbon Subnitride. Action of Halogens, of the Hydrohalogen Acids, and of Alcohols. CHARLES MOUREU and JACQUES CH. BONGRAND (*Compt. rend.*, 1920, **170**, 1025—1028. Compare A., 1914, i, 671).—The heat of combustion of carbon subnitride agrees with the equation $4C_{diamond} + N_{2gas} = C_4N_{2solid} - 138{\cdot}3$ cal. The subnitride fixes all the halogens. With an aqueous solution of hydrobromic acid, the product is *a-bromo-aβ-dicyanoethylene*,

CN·CH:CBr·CN,

m. p. 48·5—49°. Similarly, the subnitride adds on the elements of hydrogen iodide, giving *a-iodo-aβ-dicyanoethylene*, m. p. 86—87°. With hydrochloric acid, partial hydrolysis also occurs, and the product is *chloro-β-cyanoacrylamide*, m. p. 167°, the chlorine probably being attached to the a-carbon atom. When carbon subnitride is treated with absolute alcohol, it yields *a-ethoxy-aβ-dicyanoethylene*, m. p. 30·5—31°, $D^{32\cdot5}$ 1·0166, $n_D^{32\cdot5}$ 1·4677. Similar additive products are obtained with other alcohols. W. G.

Preparation of Cyanogen Chloride on a Large Laboratory Scale. T. SLATER PRICE and STANLEY J. GREEN (*J. Soc. Chem. Ind.*, 1920, **39**, 98T—101T).—The most convenient method for the preparation of cyanogen chloride on a large laboratory scale is by the action of chlorine on a dilute solution (12—15%) of hydrocyanic acid. The chlorine is forced into the solution through a porous pot, and the fine bubbles so produced bring about rapid chlorination. The heat of reaction is sufficient to distil over the cyanogen chloride into cooled receivers; the crude product contains water and hydrogen cyanide, together with traces of hydrochloric acid; methods of purification are described.

Instead of using a pure solution of hydrocyanic acid, the acid may be made in situ by the interaction of sodium cyanide and sulphuric acid solutions, the hydrocyanic acid solution thus produced being about 6% strength. On a large scale, this method suffers from the disadvantage that considerable cooling is necessary during the preparation of the solution of hydrocyanic acid.

The method described by Jennings and Scott (A., 1919, i, 526) is not practicable on a large scale, owing to the difficulty of regulating the temperature.

It is shown that the reaction between chlorine and hydrocyanic

acid proceeds quantitatively according to the equation $Cl_2 + HCN = CNCl + HCl$.

Pure cyanogen chloride has b. p. 13° (uncorr.) and m. p. −8°, D_4^0 1·207, and D_4^1 1·218. By the action of hydrogen chloride, the following effects are produced: (*a*) The cyanogen chloride is polymerised to cyanuric chloride, the reaction taking place slowly and only to any extent in the absence of water. (*b*) Hydroxylation of the cyanogen chloride to cyanic acid and carbon dioxide, and hence to ammonium chloride and carbon dioxide. This is a much more rapid reaction than (*a*), the velocity increasing with the strength of the acid. The action is complete in a few hours with 9*N*-HCl; with 2*N*-acid, the reaction is very slow, and even with 5*N*-acid takes several days. The pure substance does not undergo polymerisation, and dry chlorine and carbonyl chloride have no action on it.

In an addendum, a small-scale continuously acting apparatus is described. T. S. P.

Methylstannonic Acid and some of its Salts and Derivatives. J. G. F. DRUCE (*Chem. News*, 1920, **120**, 229—230).—In view of the suggestion that potassium hydrogen stannite has a structure similar to that of potassium formate (Hantzsch, A., 1902, ii, 289), the relationship of methylstannonic acid to acetic acid has been studied, but they are found to have little in common. The corresponding methylstannonates are precipitated on the addition of copper, zinc, nickel, or ferrous sulphates to solutions of the alkali salts. The acid is insoluble in solutions of the alkaline carbonates or in organic solvents, but soluble in mineral acids, acetic and tartaric acids. It is infusible, but when strongly heated is decomposed into stannic oxide, methane being also produced in absence of air. Stannic oxide is also produced when the acid is gently heated with ammonium nitrate. A modification of Pfeiffer and Lehnardt's method of preparing the acid (A., 1903, i, 470, 802) consists in the careful acidification of the residual solution after removal of alcohol at 40° from the product of the action of methyl iodide on an alcoholic potassium stannite solution at the ordinary temperature for three days. Methylstannoyl potassium carbonate, which is produced by Pfeiffer's process, forms crystalline platelets, the solution of which in water is alkaline in reaction and suffers decomposition either by heat or by dilute hydrochloric acid, carbon dioxide being produced in the latter case. *Aniline methylstannichloride*, $(NH_2Ph)_2H_2MeSnCl_5$, prisms, m. p. 214°, from tin methyl chloride or methylstannonic acid and aniline hydrochloride, forms an acid solution, unaltered by boiling. *Methylaniline methylstannichloride*, $(NHMePh)_2H_2MeSnCl_5$, granules, m. p. 194°. *Pyridine methylstannichloride*, $Py_2H_2MeSnCl_5$, yellow plates, m. p. 300°. J. K.

Catalytic Oxidation. I. Benzene. JOHN MORRIS WEISS and CHARLES R. DOWNS (*J. Ind. Eng. Chem.*, 1920, **12**, 228—232. Compare this vol., i, 216, 236).—An outline of investigations of

the catalytic oxidation of benzene, especially the formation of maleic acid. In this reaction, using vanadium dioxide as catalyst, temperature control is the most important factor. The apparatus employed consisted essentially of a vaporiser and mixer, a contact tube, and a condensing system; the contact tube was immersed in a metal bath kept at a definite temperature. W. P. S.

The Introduction of the Chloromethyl Group into the Aromatic Nucleus. HENRY STEPHEN, WALLACE FRANK SHORT, and GEOFFREY GLADDING (T., 1920, **117**, 510—527).

[**Freezing Points of Binary and Ternary Systems of Nitrotoluenes.**] E. CHABANIER (*Mon. Sci.*, 1920, [v], **10**, 80).—The method of determining the freezing points of component systems of nitrotoluenes described by Bell and Herty (this vol., i, 152) is the most trustworthy yet devised; but to obtain concordant results, the supercooling must not be too pronounced, since the temperature does not subsequently rise to the same extent as when there is only slight supercooling. Owing to the variable influence of supercooling, the melting-point curves thus obtained will be slightly below the true curves for binary systems. Applying the hypothesis of Bell and Herty, the eutectic points of binary mixtures of 2:3-, 2:4-, 2:5-, and 2:6-dinitrotoluenes have been calculated. The method is also applicable to the study of nitration processes. For example, direct nitration of toluene to dinitrotoluene gives mixtures of 2:4- and 2:6-dinitrotoluene, from which crystals solidifying at 66—67° can be separated, whereas by the nitration of mononitrotoluene to dinitrotoluene, a mixture solidifying at about 59° is obtained. In like manner, differences may be observed in the products obtained by nitrating toluene to trinitrotoluene directly or in three stages. C. A. M.

The Electrochemical Oxidation of *p*-Nitrotoluene and of its Isomerides. FR. FICHTER and GÉRALD BONHÔTE (*Helv. Chim. Acta*, 1920, **3**, 395—409).—Contrary to the statement of Elbs that the electrochemical oxidation of *p*-nitrotoluene does not proceed beyond the formation of *p*-nitrobenzyl alcohol (A., 1897, i, 332), it is shown that under varying conditions in acetic–sulphuric acid solution with a platinum anode, both *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid are produced (compare Coehn, *Zeitsch. Elektrochem.*, 1903, **9**, 643; Labhardt and Zschoche, A., 1902, i, 289). The alcohol owes its protection from further oxidation to the simultaneous formation of a tarry product, of low nitrogen content and phenolic in character, together with nitric acid as a result of the replacement of the nitro-group of *p*-nitrotoluene by hydroxyl. In virtue of its easy oxidisability (compare A., 1914, i, 946), this product acts as a depolariser. The acetic acid also plays a part by protecting the alcohol from the action of the nitric acid; if aqueous sulphuric acid be used, a better yield of *p*-nitrobenzoic acid is produced, and *p*-nitrobenzyl alcohol can only be isolated with difficulty. Experiments on the electrolytic oxidation

of phenol showed that the formation of carbon dioxide was greatly increased by nitric acid, but this effect was negligible when acetic acid was also present. Successively better yields of *p*-nitrobenzoic acid, without the formation of tar, are obtained by replacing *p*-nitrotoluene by *p*-nitrobenzyl alcohol or *p*-nitrobenzaldehyde, whether acetic acid be present or not. Owing to its greater oxidisability, *o*-nitrotoluene suffers complete decomposition in aqueous sulphuric acid, but in acetic-sulphuric acid gives a smaller yield of nitrobenzyl alcohol than the para-isomeride (compare Pierron, A., 1901, i, 685), with some tar, whilst the alcohol and the aldehyde may be respectively oxidised in good yield to the aldehyde and the acid. By oxidation in presence of dilute sulphuric acid, *m*-nitrotoluene also suffers complete decomposition, but *m*-nitrobenzyl alcohol cannot be detected among its oxidation products in acetic-sulphuric acid solution, since, like toluene, it yields the aldehyde, or, with sufficient current density, the acid. This may also easily be obtained in good yield from the alcohol and the aldehyde. In explanation of this difference from the ortho- and para-isomerides, it is shown that, of the series *p*-nitrotoluene, *p*-nitrobenzyl alcohol, *p*-nitrobenzaldehyde, and *p*-nitrobenzoic acid, the alcohol shows the maximum polarisation value in presence both of aqueous- and of acetic-sulphuric acids, and, in consequence, it is suggested that a peroxide of *p*-nitrobenzyl alcohol is formed which increases the oxidising effect of the anode on the higher oxidation products. If platinum be replaced by lead peroxide as anode, the alcohol is no longer obtained. When the alcohol is used as starting material, it reacts with any peroxide to form the aldehyde, and so weakens its protective action. The polarisation values of *o*- and *m*-nitrobenzyl alcohols are very small, in accordance with the smaller yields obtained of these substances.

J. K.

Formation and Decomposition of Aromatic Sulphonic Acids by Electrochemical Oxidation. Fr. Fichter, Robert Brändlin, and Ernst R. Hallauer (*Helv. Chim. Acta*, 1920, **3**, 410—422. Compare A., 1914, i, 811).—By electrolytic oxidation of ammonium 4:4′-disulphodiphenyl disulphide at a platinum anode, benzene-*p*-disulphonic acid is produced in 88% yield, but is only freed with difficulty from impurities, presumed to arise from its oxidation (compare Tonoli, *Chem. Zeit.*, 1912, **36**, 939). Experiments on the electrolytic oxidation of ammonium benzene-*p*-disulphonate itself indicated the formation of a phenolic compound as intermediate product, the final product being isolated as a *barium* salt, to which the formula $C_{12}H_4O_{16}S_3Ba_4$ is assigned with reserve. Phenol-2:5-disulphonic acid is probably an intermediate product, since on oxidation it exhibits a similar series of colour changes, probably involving the formation of catechol-4-sulphonic acid. Benzene-*m*-disulphonic acid also appears to furnish phenolic compounds (possibly catechol-4-sulphonic acid and quinolsulphonic acid), since the odour of *p*-benzoquinone is observed and the solution gives a green coloration with ferric chloride, but suffers com-

plete decomposition without offering the possibility of isolating intermediate products. J. K.

Purification of Decahydronaphthalene TETRALIN G.M.B.H. (D.R.-P. 310781; from *Chem. Zentr.*, 1920, ii, 601—602).—Incompletely hydrogenated naphthalene is treated with liquid sulphur dioxide; naphthalene and its tetra-, hexa-, and octa-hydrated derivatives readily pass into solution, whilst decahydronaphthalene is practically insoluble in this medium. H. W.

Preparation of Chlorinated Nitronaphthalenes. OSKAR MATTER (D.R.-P. 317755; from *Chem. Zentr.*, 1920, ii, 601).—The chloro-additive compounds of naphthalene are treated with nitric acid at a low temperature, and the products so formed are heated with water or with reagents which combine with acids. Thus, naphthalene dichloride and nitric acid (D 1·5) yield a *nitronaphthalene dichloride* which, when boiled with water or heated with milk of lime, passes into 8-*chloro-α-nitronaphthalene*, m. p. 93—94°; the latter is reduced by stannous chloride and hydrochloric acid to 8-*chloro-α-naphthylamine*, m. p. 88—89°. Similarly, naphthalene tetrachloride and nitric acid (D 1·5) form a resinous *nitronaphthalene tetrachloride*, which is transformed by methyl alcohol and sodium carbonate, or by benzene, methyl alcohol, and sodium hydrogen carbonate at 140—150°, into 5:8-*dichloro-α-nitronaphthalene*, m. p. 94°. 5:8-*Dichloro-α-naphthylamine*, m. p. 104—105°, is prepared by reducing the latter with tin and hydrochloric acid. H. W.

The Reduction of Nitronaphthalenesulphonic Acids. HANS EDUARD FIERZ and PAUL WEISSENBACH (*Helv. Chim. Acta*, 1920, **3**, 305—311).—The results of previous investigators have tended to show complete agreement between the nitro-derivatives of benzene and of naphthalene in their behaviour on reduction. It is now found that the reduction, whether electrolytic or by means of iron and ferrous sulphate, of 5-nitro- and 8-nitronaphthalene-2-sulphonic acid only yields the corresponding hydroxylamines (compare D.R.-P. 81621). The resulting solutions have strong reducing properties, and give red precipitates of unstable Schiff's bases when treated with formaldehyde and dimethylaniline. Complete reduction is only achieved in weakly acid solution, for example, by the use of ferrous acetate. The 5- and 8-nitronaphthalene-1-sulphonic acids, however, and also 8-nitronaphthalene-1:3:6-trisulphonic acid, may be reduced electrolytically to the amino-acids in 10% sulphuric acid solution, a current density of 200—600 amp./dm.^{2} being employed between lead electrodes.

The dissociation constants of the following acids are given: naphthalene-1-sulphonic acid, 0·18; naphthalene-2-sulphonic acid, ·25 (compare Wegscheider and Lux, A., 1909, ii, 649); 5-nitronaphthalene-1-sulphonic acid, 0·15, the 8-nitro-isomeride, 0·094;

5-nitronaphthalene-2-sulphonic acid, 0·10, the 8-nitro-isomeride 0·13; 8-nitronaphthalene-1:3:6-trisulphonic acid, 0·055. J. K.

Naphthalene-1-sulphonic Acid. HANS EDUARD FIERZ and PAUL WEISSENBACH (*Helv. Chim. Acta*, 1920, **3**, 312—318).—It is shown that the sulphonation of naphthalene, even at low temperatures, always results in the formation of some naphthalene-2-sulphonic acid, for example, at least 2% at 0° (Euwes, A., 1909, i, 707). The determination of the proportion is based on the fact that the 1-acid crystallises from aqueous solution as a dihydrate whilst the 2-acid forms a trihydrate. Apparently the process of sulphonation consists in the formation of a molecular compound which undergoes decomposition into either the 1- or the 2-acid according to the prevailing external conditions. Naphthalene-1-sulphonic acid separates from aqueous solution in the form of tiny non-deliquescent columns, surmounted by pyramids,

$$C_{10}H_7\cdot SO_3H,2H_2O,$$

m. p. 90°, which cannot be completely dehydrated without decomposition. The *ammonium* salt, $C_{10}H_7\cdot SO_3\cdot NH_4$, pearly leaflets; the *lead* salt, $(C_{10}H_7SO_3)_2Pb,3H_2O$, lustrous leaflets, is converted into the monohydrate at 85°; the *zinc* salt ($6H_2O$), thin leaflets; the *cobalt* salt ($6H_2O$), lustrous, pale red leaflets, is bluish-violet when anhydrous; the *nickel* salt ($6H_2O$), lustrous, light green leaflets, turns yellow and becomes anhydrous at 185°; the *copper* salt ($6H_2O$), turquoise-blue leaflets, is dehydrated and turned yellow at 180°; the *cadmium* salt ($6H_2O$) and the *zinc* salt ($6H_2O$) form leaflets. The strontium salt crystallises as a dihydrate. J. K.

Action of Aqueous Sodium Hydroxide on the α-Naphthylaminesulphonic Acids. HANS EDUARD FIERZ (*Helv. Chim. Acta*, 1920, **3**, 318—329).—Diagrams of curves are given expressing the tabulated results of a quantitative study of the proportions of the products obtained by the treatment of the α-naphthylamine-sulphonic acids with varying strengths of sodium hydroxide solution at different temperatures. The following products are obtained, the figures in brackets indicating the maximum proportion observed, with the corresponding temperature and strength of alkali employed, time of action in all cases being three hours; from α-naphthylamine-4-sulphonic acid: α-naphthol (59%); α-naphthol-4-sulphonic acid (54%; 280°, 10%), 1:4-dihydroxynaphthalene (traces), but no α-naphthylamine; from α-naphthylamine-5-sulphonic acid, 1:5-dihydroxynaphthalene (60·2%; 290°, 30 or 50%), 5-amino-α-naphthol (52·4%; 250°, 30%), α-naphthylamine (7·8%; 300°, 50%), and probably a little α-naphthol-5-sulphonic acid; from α-naphthylamine-6-sulphonic acid, α-naphthol-5(?)-sulphonic acid (49%; 260°, 20%), 1:6-dihydroxynaphthalene (17%; 260°, 50%), α-naphthylamine (0·3%; 260°, 20 or 50%), unchanged acid (37%; 260°, 20%) and traces of 5-amino-β-naphthol; from α-naphthylamine-7-sulphonic acid, α-naphthol-7-sulphonic acid (40%[?]; 260°, 50%), 8-amino-β-naphthol (37·7%; 260°, 50%), 1:7-dihydroxynaphthalene (3%; 260°, 20%), unchanged acid (55%;

260°, 20%); from α-naphthylamine-8-sulphonic acid, 1:8-dihydroxynaphthalene (46·6% [70% by very rapid heating]; 300°, 10%), α-naphthylamine (32·5%), α-naphthol-8-sulphonic acid, and traces of 8-amino-α-naphthol. Some naphthalene is always produced when naphthalene-1- or -2-sulphonic acids are fused with sodium hydroxide solution (compare Willson and Meyer, A., 1915, i, 232).

J. K.

Preparation of Hexanitrodiphenylamine and its Use as a Primer in Shell Charges. JOHN MARSHALL (*J. Ind. Eng. Chem.*, 1920, **12**, 336—340).—Hexanitrodiphenylamine is more stable than tetranitromethylaniline or tetranitroaniline, and is superior to trinitrotoluene as a detonator. It may be prepared on a large scale by a modification of Carter's method (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1913, 205) of nitrating aniline. In the first stage, two mols. of aniline and one mol. of chloronitrobenzene are emulsified with hot water, and the temperature raised to 80° for an hour. Dinitrodiphenylamine is precipitated in clusters of red needles melting at 148° to 152°. This is converted into tetranitrodiphenylamine by nitration with a suitable mixture of nitric and sulphuric acids, first at 70° and then at 80° to 90°, yielding a brownish-yellow, amorphous mass containing small amouuts of higher nitration products. The final nitration of this material is effected at 90°, and yields up to 80% of the theoretical amount of hexanitrodiphenylamine in yellow crystals melting at 238·5—239·5°. The method of nitrating dinitrodiphenylamine in one operation, suggested by Hoffmann and Dame (A., 1919, i, 394), is less suitable, since it yields au amorphous material melting at 238°. The absolute density of the crystalline product was 1·653. [See, further, *J. Soc. Chem. Ind.*, 1920, 429A.] C. A. M.

Preparation of Diarylurethanes. CHEMISCHE FABRIKEN VORM WEILER TER MEER (D.R.-P. 306316; from *Chem. Zentr.*, 1920, i, 491—492).—The diarylamine or its hydrochloride (one molecule) is warmed with one or more molecules of ethyl chloroformate in the presence or absence of a solvent until hydrogen chloride ceases to be evolved. When only one molecule of diarylamine is employed, a quantitative conversion of diarylamine into urethane is effected, and free hydrogen chloride is evolved. The preparation of diphenylurethane from diphenylamine and chloroformic ester is particularly described. H. W.

Ferribenzhydroxamic Acid Compounds. R. F. WEINLAND and GERTRUD BAIER (*Ber.*, 1920, **53**, [*B*], 685—696).—Addition of aqueous ferric chloride to a solution of sodium benzhydroxamate in water yields the sparingly soluble ferribenzhydroxamate,

$$CPh{<}{\begin{matrix}O-\tfrac{1}{3}Fe\\ \vert\\ N\cdot OH\end{matrix}},1\cdot5H_2O,$$

reddish-brown rods or six-sided platelets from 96% alcohol, needles from more dilute alcohol. The substance behaves as an internally

complex salt; it dissolves readily in aqueous solutions of all types of bases and in dilute acids, apparently with formation of salts, which can only exist in solution, since the latter ultimately deposits the original material. From alcoholic solutions of ferric chloride, *benzhydroxamic acid and pyridine* (or quinoline), the following series of *salts* has been prepared [in the formulation of which BzxH represents the benzhydroxamic acid molecule and Bzx the radicle PhC(:N·OH)·O]: (i) rectangular, violet platelets,

$$\left[Fe_{BzxH}^{Py_5}\right]\left[Fe_{(Bzx)_2}^{Cl_4}\right],5H_2O;$$

(ii) pale violet, irregular, six-sided platelets, $\left[Fe_{Bzx}^{Py_5}\right]\left[Fe\begin{matrix}Cl_4\\Bzx\\Py\end{matrix}\right]$, which are converted by water into ferribenzhydroxamate; (iii) the cherry-red salts $FeCl_3,BzxHPy$ and $FeCl_3,BzxH$ Quinoline, which are soluble in water and are to be regarded simply as the pyridine and quinoline salts of a trichlorobenzhydroxamatoferri-acid, $\left[Fe_{Bzx}^{Cl_3}\right]H$; (iv) dark red, shining powder,

$$\left[Fe_{BzxH}^{Cl_5}\right]\left[Fe_{Bzx}^{Py_2}\right]_3\left[Fe_{BzxH}^{Cl_4}\right]+12H_2O;$$

(v) dark red salt, $[FeCl_6]\left[Fe_{Bzx_2}^{Quinoline_2}\right]_3\left[Fe_{BzxH}^{Cl_4}\right]+6H_2O$.

(vi) reddish-brown needles, $2\left[Fe\begin{matrix}Py\\Cl\\Bzx_2\end{matrix}\right],\left[Fe_{Bzx_2}^{Py}\right]+6H_2O$. The preparation of the individual salts is effected by suitably varying the relative proportions of the components; for details, the original must be consulted. H. W.

Preparation of Dinitrophenol. OSWALD SILBERRAD (Brit. Pat. 140955).—2:4-Dinitrophenol is obtained by suspending 100 parts of *p*-nitrosophenol in a solution of 200 parts of sodium nitrate in 350 parts of water and running the mixture into 480 parts of 50% sulphuric acid at 70—80°, the temperature being finally raised to and maintained for six hours at, 95°. The yield amounts to 135 parts of dinitrophenol, representing 130% on the phenol initially employed. If desired, nitric acid (D 1·2) may be substituted for the sodium nitrate and sulphuric acid. G. F. M.

Preparation of Pyrogallol. NITRITFABRIK AKT.-GES. (Brit. Pat. 140694).—Pyrogallol is obtained in nearly theoretical yield by heating solutions or suspensions of tannic or gallic acids at temperatures above 160° in an autoclave, with a proportion of alkali or alkaline earth, etc., hydroxides or carbonates not materially exceeding twice the amount required to effect substitution of the hydrogen atoms of the carboxyl groups initially present and those formed by hydrolysis, if any. G. F. M.

The Valency Problem of Sulphur. III. H. LECHER (*Ber.*, 1920, **53**, [*B*], 577—590. Compare A., 1915, i, 532; 1916, i, 41).—In previous communications (A., 1915, i, 532; 1916, i, 41), evidence has been brought forward to show that diphenyl disulphide and di-*p*-dimethylaminodiphenyl disulphide are not appreciably dissociated into free radicles, since their solutions obey Beer's law. This method of attacking the problem is not, however, sufficiently accurate to enable conclusions to be drawn as to the possibility of a slight dissociation. A different mode of working has now been adopted, and it is shown that a solution of molar amounts of diphenyl disulphide and di-*o*-nitrodiphenyl disulphide in boiling xylene is unchanged after three hours, and in benzene at 200° is unaltered after six hours, and that the same is true of equivalent solutions of *o*-nitrodiphenyl disulphide in the same solvents. From these experiments, the conclusion is drawn that the solutions of the latter substance cannot contain any free radicle, and, whilst a partial dissociation of one of the symmetrical disulphides is not absolutely excluded, it is highly improbable that such is actually the case.

Diphenyl disulphide, di-*p*-dimethylaminodiphenyl disulphide, di-*o*-nitrodiphenyl disulphide, and *o*-nitrodiphenyl disulphide exhibit thermochromic properties, darkening when heated in the crystalline or molten condition or when in solution, and returning to their original colour when cooled. The phenomenon is exhibited most strongly by the dimethylamino-, least strongly by the nitro-derivatives. It does not appear to depend on the formation of free radicles, and is not a specific property of the disulphide group, since it is also exhibited by *o*-nitrodiphenyl sulphide. It may possibly be partly attributable to the presence of the nitro-group, since nitrobenzene is itself thermochromic.

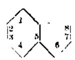
The dissociation of mercury phenylmercaptide into mercury and diphenyl disulphide, $Hg(SPh)_2 \rightleftharpoons Hg + PhS{\cdot}SPh$, does not appear to be attributable to a preliminary detachment of the SPh-radicle, since *o*-nitrodiphenyl disulphide is found to react with mercury under conditions which preclude the presence of the free radicle; the products of the action are diphenyl disulphide, di-*o*-nitrodiphenyl disulphide, and *mercury o-nitrophenylmercaptide*, small, yellow, very electric needles, m. p. 231° (decomp.) after softening at 222° and darkening at 228°.

o-*Nitrodiphenyl disulphide*, $NO_2{\cdot}C_6H_4{\cdot}S{\cdot}SPh$, long, yellow crystals, m. p. 55°, is smoothly prepared by the action of *o*-nitrochlorothiolbenzene (Zincke and Farr, A., 1912, i, 763) on phenylmercaptan in dry ethereal solution. H. W.

Reduction of Organic Disulphides by Alkali Mercaptides. H. LECHER (*Ber.*, 1920, **53**, [*B*], 591—593).—The author has attempted to prepare *o*-nitrodiphenyl disulphide, $NO_2{\cdot}C_6H_4{\cdot}S{\cdot}SPh$, by the action of *o*-nitrochlorothiolbenzene (Zincke and Farr, A., 1912, i, 763) on sodium phenyl sulphide, but has thereby obtained

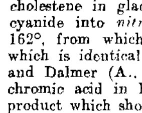
mainly a mixture of the *s*-diphenyl disulphide and di-*o*-nitrodiphenyl disulphide. The *as*-disulphide is shown to be formed primarily and to be immediately reduced by the sodium phenyl sulphide to diphenyl disulphide and sodium *o*-nitrophenyl mercaptide, $NO_2 \cdot C_6H_4 \cdot S \cdot SPh + PhSNa = NO_2 \cdot C_6H_4 \cdot SNa + PhS \cdot SPh$; the latter then reacts with *o*-nitrochlorothiolbenzene to yield di-*o*-nitrodiphenyl disulphide. H. W.

Cholesterol. XXIX. Certain Derivatives of Cholestene and ψ-Cholestene and the Proof of the Existence of a Methylene Group adjacent to a Double Bond in Cholesterol. A. WINDAUS (*Ber.*, 1920, **53**, [*B*], 488—497).—Cholestene and ψ-cholestene have been converted into three different monoketones, in which the carbonyl group is in the positions 6, 7, and 8 respectively when the numbering shown in the annexed scheme is adopted.



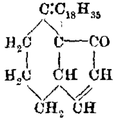
Nitrocholestene, leaflets, m. p. 117—118° (Mauthner and Suida give m. p. 105°), is prepared in 75% yield by the action of fuming nitric acid (D 1·52) on a solution of cholestene in glacial acetic acid, and is converted by potassium cyanide into *nitrocholestene hydrocyanide*, long needles, m. p. 162°, from which cholestan-7-one, m. p. 98—99°, is prepared, which is identical with heterocholestanone described by Windaus and Dalmer (A., 1919, i, 204). The latter, when oxidised by chromic acid in hot glacial acetic acid solution, yields an acid product which shows no tendency to crystallise, but which, on distillation under diminished pressure, gives an unsaturated hydrocarbon, $C_{25}H_{42}$ or $C_{25}H_{44}$ [identical with the product obtained by Windaus and Resan (A., 1914, i, 682) by the oxidation of cholestene with permanganate], transformable by catalytic hydrogenation into a saturated hydrocarbon, m. p. 45° (see later). Similarly, 4-chlorocholestane-7-one is converted by chromic acid into a non-crystalline acid, from which an unsaturated hydrocarbon, $C_{25}H_{40}$ or $C_{25}H_{42}$, m. p. 76°, is obtained, identical with the product isolated by Windaus and Resan (*loc. cit.*) by the distillation of the acidic oxidation compounds of cholesteryl acetate. Catalytic hydrogenation in ethereal solution converts the latter mainly into a saturated hydrocarbon, m. p. 80°, whilst in glacial acetic acid solution the hydrocarbon, m. p. 45° (see above), is formed.

Nitro-ψ-cholestene, $C_{27}H_{45}O_2N$, has m. p. 70°, and is converted by zinc dust and acetic acid into *cholestan-6-one*, m. p. 98—99° (*oxime*, slender needles, m. p. 205°). The latter is reduced by amalgamated zinc and hydrochloric acid to cholestane, m. p. 79—80°, and is oxidised by fuming nitric acid to a dicarboxylic *acid* (annexed formula), m. p. 240°.



The oxidation of cholestene by a considerable excess of chromic acid in glacial acetic acid solution leads to the production of small

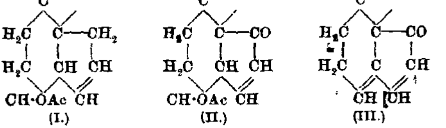
amounts (*ca.* 10%) of the unsaturated ketone, *ketocholestene* (annexed formula), plate-like crystals, m. p. 145° (*semicarbazone*, small needles, m. p. 225° [decomp.]). The constitution of the latter follows from its catalytic hydrogenation to *cholestane-8-one*, m. p. 108—109°, which is found to differ from either cholestane-6- or -7-one, but to be oxidised by fuming nitric acid to a dicarboxylic acid, $C_{27}H_{46}O_4$, identical with that obtained from cholestane-7-one, thus showing the keto-group to be present in the position 8. Hence, cholestene must contain the methylene group in juxtaposition to the group -CH:CH-, and this arrangement must also be present in the cholesterol molecule.



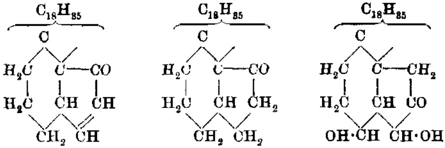
H. W.

Cholesterol. XXX. Oxidation of Cholesteryl Acetate. A. WINDAUS and E. KIRCHNER (*Ber.*, 1920, **53**, [*B*], 614—621).—The oxidation of cholesteryl acetate (I) with chromic acid (Mauthner and Suida, A., 1897, i, 31; Windaus and Resau, A., 1915, i, 677) yields a mixture of β-oxycholestenyl acetate and a substance, $C_{29}H_{48}O_4$, the constitutions of which have not been satisfactorily elucidated. Attempts have been made in this direction by Windaus and Resau (*loc. cit.*), but their arguments are based on a formula for cholesterol since disproved. Revision of the latter (preceding abstract) has enabled the problem to be solved.

β-Oxycholestenyl acetate (II) is readily hydrolysed to the simply unsaturated keto-alcohol oxycholestenol, which readily loses water and yields the doubly unsaturated ketone, ketocholesterylene (III). The latter, when submitted to step-wise catalytic hydrogenation, first absorbs two atoms of hydrogen, and gives the previously described ketocholestene (IV), and then reacts with a further two atoms to yield cholestane-8-one (V) (*loc. cit.*). The same product is ultimately obtained when ψ-cholesterol (obtained from ketocholesterylene by means of sodium and alcohol) is first oxidised to the unsaturated ketone, ψ-cholestenone, and then catalytically hydrogenated. The oxidation of cholesteryl acetate is therefore precisely analogous to that of cholestene, the methylene group adjacent to the double bond being converted into the keto-group. The individual products are therefore formulated in the following manner:



(I.) (II.) (III.)



(IV.) (V.) (VI.)

It is further shown that β-oxycholestenyl acetate can be reduced by hydrogen in the presence of spongy palladium to *ketocholestanyl acetate*, needles, m. p. 142—143°, which, on hydrolysis, yields *cholestane-8-one-4-ol*, pearly leaflets, m. p. 156—157°; the latter is oxidised by chromic acid in the presence of acetic acid to *cholestane-4 : 8-dione*, needles, m. p. 186—187°, the *dioxime* of which has m. p. 281° (decomp.).

The substance, $C_{29}H_{48}O_4$, is the monoacetyl derivative of a cholestane-one-diol, which is now shown to be *iso*cholestane-7-one-4:5-diol (VI), since, when cautiously oxidised, it passes into the previously described *iso*cholestane-4:7-dione-6-ol, which is successively convertible into cholestene-4:7-dione and cholestane-4:7-dione. H. W.

Syntheses with the Aid of Monochloromethyl Ether. IV. The Condensation of Ethyl Benzylsodiomalonate and Monochloromethyl Ether. John Lionel Simonsen (T., 1920, **117**, 564—569).

The Preparation of *cyclo*Heptane-1 : 1-diacetic Acid. James Nelson Edmund Day, George Armand Robert Kon, and Arnold Stevenson (T., 1920, **117**, 639—646).

Derivatives of α-Arylphthalides and their Conversion into Anthracene Derivatives. A. Bistrzycki and S. Zen-Ruffinen (*Helv. Chim. Acta*, 1920, **3**, 369—391. Compare A., 1899, i, 151).—6-Hydroxy-*m*-tolylphthalide, $CO<\overset{O}{\underset{C_6H_4}{}}>CH\cdot C_6H_3Me\cdot OH$, m. p. 164·5—165·5° (Winkler, *Diss.*, Freiburg [Switzerland], 1901), is best prepared by the condensation of *o*-phthalaldehydic acid with *o*-cresol in presence of 73% sulphuric acid; it yields a *benzoyl* derivative, $C_{22}H_{16}O_4$, m. p. 123—124°; ethylation gives its *ethyl ether*, $C_{17}H_{16}O_3$, m. p. 96·5—97·5°; its *methyl ether*, $C_{16}H_{14}O_3$, m. p. 124·5—125·5°, is formed from *o*-phthalaldehydic acid and *o*-tolyl methyl ether; its 5′-*bromo*-derivative, $C_{15}H_{11}O_3Br$, m. p. 185—186°, gives an *acetyl* derivative, $C_{17}H_{13}O_4Br$, m. p. 131—132°; its 5′-*nitro*-derivative, $C_{15}H_{11}O_5N$, has m. p. 182°. 6′-*Hydroxyphenyl*-m-*tolyl-methane-2-carboxylic acid*, $OH\cdot C_6H_3Me\cdot CH_2\cdot C_6H_4\cdot CO_2H$, m. p. 215—216° (*silver* salt, $C_{15}H_{13}O_3Ag$), obtained from the above phthalide by reduction with zinc dust and sodium hydroxide, is

converted by cold sulphuric acid into *2-hydroxy-3-methyl-9-anthrone*, $C_6H_4<\substack{CO\\CH_2}>C_6H_2Me\cdot OH$, glistening prisms, m. p. 276—277°, which does not fluoresce in solution. It dissolves in cold potassium hydroxide solution, and by saturating the solution at 0° with carbon dioxide, a yellow precipitate, probably of the isomeric anthranol, is produced. By acetylation, the anthrone yields *2 : 9-diacetoxy-3-methylanthracene*,

$$C_6H_4<\substack{C(OAc)\\CH}>C_6H_2Me\cdot OAc,$$

leaflets, m. p. 171—172°, which shows a blue fluorescence in acetic acid solution, and on oxidation with chromic acid gives *2-acetoxy-3-methylanthraquinone*, $C_6H_4<\substack{CO\\CO}>C_6H_2Me\cdot OAc$, needles, m. p. 177°, from which 3-hydroxy-2-methylanthraquinone, m. p. 298·5° (Fraude, 1879), is obtained by hydrolysis. *3-p-Hydroxy-m-methoxyphenylphthalide*, $CO<\substack{O\\C_6H_4}>CH\cdot C_6H_3<\substack{OH\\OMe}$, m. p. 110·5—112·5°, from *o*-phthalaldehydic acid and guaiacol, gives an *acetyl* derivative, $C_{17}H_{14}O_5$, m. p. 142—143°, and, by reduction, *4′-hydroxy-3′-methoxydiphenylmethane-2-carboxylic acid*,

$$OH\cdot C_6H_3(OMe)\cdot CH_2\cdot C_6H_4\cdot CO_2H,$$

m. p. 150—151° (*silver* salt, $C_{15}H_{13}O_4Ag$). *2-Hydroxy-3-methoxy-9-anthrone*, $C_6H_4<\substack{CO\\CH_2}>C_6H_2<\substack{OH\\OMe}$, m. p. 211—213°, from the acid just mentioned, shows no fluorescence in solution, but dissolves in cold potassium hydroxide solution, and, on acetylation, gives *2 : 9-diacetoxy-3-methoxyanthracene*, $C_6H_4<\substack{C(OAc)\\CH}>C_6H_2<\substack{OAc\\OMe}$, m. p. 158·5—160·5°, from which *2-acetoxy-3-methoxyanthraquinone*, $C_6H_4<\substack{CO\\CO}>C_6H_2<\substack{OAc\\OMe}$, m. p. 200·5—201·5°, is obtained by oxidation. This compound furnishes hystazarin monomethyl ether on hydrolysis. *3-mp-Dimethoxyphenylphthalide*,

$$CO<\substack{O\\C_6H_4}>CH\cdot C_6H_3(OMe)_2,$$

m. p. 144—145°, from *o*-phthalaldehydic acid and veratrole, suffers rupture of the lactonic ring when boiled in alcoholic solution with potassium hydroxide, and the resulting solution, on oxidation with potassium permanganate, gives *o*-3′ : 4′-dimethoxybenzoylbenzoic acid (Lagodzinski, A., 1905, i, 82). By reduction of the phthalide, only a small quantity of the expected dimethoxydiphenylmethanecarboxylic acid is produced. The condensation of opianic acid with *o*-cresol to *6′-hydroxy-m-tolylmeconine*,

$$CO<\substack{O\\C_6H_2(OMe)_2}>CH\cdot C_6H_3Me\cdot OH,$$

m. p. 181°, acetyl derivative, m. p. 137° (Winkler), is best carried out in presence of sulphuric acid; its *methyl ether*, $C_{18}H_{18}O_5$, m. p. 117·5—119°, may be obtained by methylation or from opianic

acid and *o*-tolyl methyl ether, and when boiled with dilute potassium hydroxide solution undergoes to a slight extent rupture of the lactonic ring. Neither the parent compound nor its methy ether could be converted into a diphenylmethanecarboxylic aci by reduction. This was also the case with 3-p-*hydroxy*-m-*methoxy meconine*, $CO<\overset{O}{C_6H_2(OMe)_2}>CH\cdot C_6H_3<^{OMe}_{OH}$, m. p. 164—166° 3-mp-*dimethoxyphenylmeconine*, m. p. 120·5—121·5°, yield tetramethoxy-*o*-benzoylbenzoic acid (Bentley and Weizmann, T. 1908, **93**, 437) on oxidation; 3-*orcylmeconine*,

$$CO<\overset{O}{C_6H_2(OMe)_2}>CH\cdot C_6H_2Me(OH)_2,$$

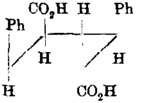
m. p. 223—225°; 3-p-*dimethylaminophenylmeconine*,

$$CO<\overset{O}{C_6H_2(OMe)_2}>CH\cdot C_6H_4\cdot NMe_2,$$

m. p. 132·5—134·5° (hydrochloride, needles), from opianic aci and dimethylaniline in presence of anhydrous oxalic acid, can als not be reduced by zinc dust and sodium hydroxide. Bistrzycki' 2-hydroxyanthranol (A., 1899, i, 151) is really 2-hydroxy-9 anthrone, $C_6H_4<^{CO}_{CH_2}>C_6H_3\cdot OH$, and, similarly, 2:3′:4′-trimeth oxydihydroanthrone is 3:4:7-trimethoxy-9-anthrone. 3-(*Nitro-β hydroxynaphthyl*)-*phthalide*, $CO<\overset{O}{C_6H_4}>CH\cdot C_{10}H_5<^{NO_2}_{OH}$, decomp at 130·5°, is obtained by nitrating β-hydroxynaphthylphthalide.

J. K.

Truxillic Acids. II. R. Stoermer and E. Emmel (*Ber.*, 192(**53**, [*B*], 497—508. Compare Stoermer and Foerster, A., 191! i, 444).—Further investigation of ε-truxillic acid leads the author to the conclusion that it is an unusually stable *trans*-acid (annexe formula), the view being maintained that th truxillic acids and the *iso*truxillic acid a structural and not stereo-isomerides.



ε-Truxillic acid, long, colourless needle m. p. 192° (identical with Hesse's β-coca acid), is conveniently prepared by protracte heating of α-truxillic acid with alkali hyd oxide. It is not affected by prolonged heatin or by drastic treatment with hydrochloric acid. Attempts to co vert it into an internal anhydride were unsuccessful, but, by th action of acetic anhydride on the acid at 200—210°, or of pho phoryl chloride on the potassium salt, a non-crystalline anhydric of high molecular weight is obtained, which, however, is reconverte by water into ε-truxillic acid. The nature of the product is co firmed by its conversion by ethyl alcohol into *ethyl hydroge ε-truxillate*, and by aniline into *ε-truxilldianilide*, m. p. 284°, an *ε-truxillanilic acid*, needles, m. p. 293°.

The following derivatives of ε-truxillic acid are described: th *barium* and *calcium* salts, which are less soluble in hot than in co water; methyl ester, m. p. 64°; *ethyl* ester, m. p. 34°; *chlorid*

n. p. 106—107°; *diamide*, small, transparent needles, m. p. 240°; *etramethyldiamide*, m. p. 190°; *dianilide*, slender, silky needles, ı. p. 284°.

The following investigations have been carried out in connexion ıith attempts to convert the truxillic acids into *cyclo*butanetetra-arboxylic acids (*loc. cit.*), but success has not been thus far chieved. Dinitro-γ-truxillic acid, m. p. 293°, is most conveniently btained by the action of fuming nitric acid (D 1·5) on the -anhydride, and is converted by acetic anhydride into dinitro-γ-uxillic anhydride, small prisms, m. p. 229°. The acid is con-erted in the usual manner into *methyl dinitro-γ-truxillate*, silky eedles, m. p. 194°, *ethyl dinitro-γ-truxillate*, glassy needles, m. p. 46°, and *dinitro-γ-truxillyl chloride*, yellow prisms, m. p. 204°. he latter readily yields the corresponding *diamide*, pale yellow ystals, m. p. 280°, *tetramethyldiamide*, m. p. 276°, and dianilide, ı. p. 261°. Dinitro-γ-truxillic anhydride is transformed by niline, according to conditions, either into *dinitro-γ-truxillanilic id*, m. p. 265°, or the corresponding dianilide; in contrast to the haviour of β-*iso*truxillic anhydride, it could not be caused to eld an anil or a fluorescein derivative. With ethyl alcohol, it ves *ethyl hydrogen dinitro-γ-truxillate*, long needles, m. p. 76—177°.

Ethyl dinitro-γ-truxillate is reduced by hydrogen in the presence palladium to *ethyl diamino-γ-truxillate*, m. p. 162—163°; efinite substances could not be isolated from the products of the idation of the hydrolysed ester by permanganate in acid or kaline solution. H. W.

Bis-tropic Acids. JULIUS VON BRAUN and LUDWIG NEUMANN (*Ber.*, 1920, **53**, [*B*], 594—601).—The experiments were under-ken with the pharmacologically interesting object of determining e extent to which it is possible to introduce doubly the group $CH(CH_2\cdot OH)\cdot CO_2H$, characteristic of tropic acid, into the omatic nucleus. Unfortunately, the derivatives from *m*-xylene hibit little tendency to crystallise, and cannot be distilled with-ıt decomposition, whilst the crystalline compounds from *o*- and xylenes could not be prepared on a sufficiently large scale owing the prevalent scarcity of the parent hydrocarbons.

Ethyl *p*-phenylenediacetate readily condenses with ethyl formate the presence of sodium and ether to yield *ethyl bishydroxy-ethylene-p-phenylenediacetate*, $C_6H_4[C(:CH\cdot OH)\cdot CO_2Et]_2$, m. p. .2—114°; the substance is immediately and completely soluble in lute alkali or sodium carbonate solution, and in alcoholic solu-on gives an immediate, very dark bluish-violet coloration with rric chloride. It readily yields a pale green, basic *copper* salt, d is transformed by aniline into the corresponding *dianilide*, $H_4[C(:CH\cdot NHPh)\cdot CO_2Et]_2$, crystalline powder, m. p. 143°. The *nzoyl* derivative has m. p. 186—187°. With phenylcarbimide, e ester yields diphenylcarbamide, owing to the unexpectedly ady elimination of water. Unlike ethyl and methyl formyl-

phenylacetates, the ester appears to have absolutely no tendency to pass into the ketonic form, and this fact appears to afford a certain amount of evidence against the aldo-enolic formulation of the former. An ethereal solution of the *p*-phenylene ester is readily reduced by activated aluminium (yield, 50%) to *ethyl* p-*phenylenebistropate* [*ethyl bishydroxymethyl*-p-*phenylenediacetate*], $C_6H_4[CH(CH_2 \cdot OH) \cdot CO_2Et]_2$, m. p. 65—66°, which is hydrolysed by aqueous barium hydroxide to p-*phenylenebistropic acid*, shining leaflets, m. p. 93—94°.

Ethyl m-*phenylenediacetate*, colourless liquid, b. p. 196—198°/14 mm., condenses readily with ethyl formate, yielding a product which gives an intense bluish-violet coloration with ferric chloride, but which could only be obtained as a rather viscous, non-crystallisable oil, which decomposed when distilled even in a cathode vacuum. The reduction product is also an oil, whilst the acid corresponding with it could only be obtained as a sticky mass.

Ethyl diformyl-o-*phenylenediacetate*, prepared in the same manner as, but rather more readily than, the corresponding para-derivative, forms dark yellow crystals, m. p. 77—78°, and behaves solely as an enolic form. It is readily soluble in sodium carbonate, gives an intense bluish-green coloration with ferric chloride, a moss-green *copper* salt, and a dark yellow *anilide*, m. p. 200°. Like the para-compound, it loses water and forms diphenylcarbamide when treated with phenylcarbimide. Unlike the para-compound and all other formyl derivatives, however, it gives an intense permanganate-like coloration when its solution in alkali is shaken with benzoyl chloride, and an amorphous, violet precipitate rapidly separates. H. W.

Formation and Stability of Associated Alicyclic Systems. I. A System of Nomenclature, and some Derivatives of Methane-II-*cyclo*propane and of Methane-III-*cyclo*propane. RICHARD MOORE BEESLEY and JOCELYN FIELD THORPE (T., 1920, **117**, 591—620).

Preparation of Mellitic Acid. RICHARD LORENZ and JULIUS HAUSMANN (D.R.-P. 318200; from *Chem. Zentr.*, 1920, ii, 492).—Mixtures of finely divided carbon or soot with tar, pressed into rods or plates and subsequently heated in the absence of air, are subjected to anodic oxidation in an alkaline electrolyte; the liberated hydrogen may be obtained as by-product if a diaphragm is used. Soot may be replaced by other finely divided varieties of carbon, such as wood charcoal, lamp-black, or gas carbon, either alone or in admixture with soot. Solutions of sodium or potassium hydroxide, or of alkali carbonates or hydrogen carbonates, may be used as electrolytes. H. W.

Some Derivatives of 2 : 4-Dinitrobenzaldehyde. ALEXANDER LOWY and BLAINE B. WESCOTT (*J. Amer. Chem. Soc.*, 1920, **42**, 849—856).—A number of condensation products of 2:4-di-

nitrobenzaldehyde with aromatic amines are described. No evidence of stereoisomerism could be observed among them, and attempts to isolate the intermediate additive compounds were unsuccessful.

2:4-*Dinitrobenzylidene*-m-*toluidine*, $C_6H_3(NO_2)_2\cdot CH\colon N\cdot C_6H_4Me$, yellow needles, m. p. 130°; 2:4-*dinitrobenzylidene*-m-4-*xylidine*, $C_6H_3(NO_2)_2\cdot CH\colon N\cdot C_6H_3Me_2$, yellow needles, m. p. 210·5°; 2:4-*dinitrobenzylidene-3-nitro*-p-*toluidine*,

$$C_6H_3(NO_2)_2\cdot CH\colon N\cdot C_6H_3Me\cdot NO_2,$$

yellow needles, m. p. 195°; 2:4-*dinitrobenzylidene-ψ-cumidine*, $C_6H_3(NO_2)_2\cdot CH\colon N\cdot C_6H_2Me_3$, yellow needles, m. p. 186·5°; *sodium* 2:4-*dinitrobenzylidenesulphanilate*,

$$C_6H_3(NO_2)_2\cdot CH\colon N\cdot C_6H_4\cdot SO_3Na,H_2O,$$

pale yellow crystals, decomposing at 249°; *sodium* 2:4-*dinitrobenzylidenemetanilate* ($3H_2O$), yellow needles, decomposing at 185°; *sodium* 2:4-*dinitrobenzylidenenaphthionate*,

$$C_6H_3(NO_2)_2\cdot CH\colon N\cdot C_{10}H_6\cdot SO_3Na,\tfrac{1}{2}H_2O,$$

orange needles, decomposing at 248°. By condensation with dimethylaniline, 2:4-dinitrobenzaldehyde yields a green dye, doubtless a derivative of malachite-green. J. K.

Constitution of the Methylethyl*cyclo*hexanone prepared by Ethylation of 1-Methyl*cyclo*hexan-6-one. A. HALLER and R. CORNUBERT (*Compt. rend.*, 1920, **170**, 973—976).—The compound previously prepared by the ethylation of 1-methyl*cyclo*hexan-6-one in the presence of sodamide (compare A., 1913, i, 984) is shown to be 1-ethyl-1-methyl*cyclo*hexan-6-one. Like dimethyl*cyclo*hexanone (compare this vol., i, 390), it gives a benzylidene derivative, which is 5-*benzylidene*-1-*methyl*-1-*ethyl*cyclo*hexan*-6-*one*, m. p. 78—78·5°, and a *compound*, $C_{23}H_{26}O_2$, m. p. 148—150°. W. G.

Hydroxycarbonyl Compounds. IV. Synthesis of Aspidinol. P. KARRER and FR. WIDMER (*Helv. Chim. Acta*, 1920, **3**, 392—395. Compare A., 1919, i, 160, 592, 594).—By condensation of butyronitrile with methyl phloroglucinol β-monomethyl ether in presence of hydrogen chloride, a mixture of two ketones, $OMe\cdot C_6HMe(OH)_2\cdot COPr^a$, was produced, which can be resolved into its components by fractional crystallisation from light petroleum. The less soluble, m. p. 140—141°, gave a green colour with ferric chloride, and its identity with aspidinol (Böhm, A., 1902, i, 37) was established by direct comparison. The more soluble, needles, m. p. 116·5°, gave a deep brownish-red colour with ferric chloride, and was called *ψ-aspidinol*. The two compounds are doubtless the 3- and the 5-butyryl derivatives of the original compound, of which aspidinol has been considered to be the 3-butyryl derivative (Böhm); but this would be contrary to the rule that in such compounds the isomeride with the ketonic group in the para-position to the methoxyl group has a lower melting

point and a greater solubility in light petroleum than the ortho-isomeride (Karrer, A., 1919, i, 592). The distribution of the formulæ between the two compounds is therefore left undecided.

J. K.

The Ketimines: Formation by Catalytic Reduction of Oximes. GEORGES MIGNONAC (*Compt. rend.*, 1920, **170**, 936—938).—Ketoximes may be reduced in solution in absolute alcohol in the presence of reduced nickel by shaking the solution with hydrogen under atmospheric pressure. The action should be stopped when one molecule of hydrogen has been absorbed for one molecule of oxime. The resulting ketimines undergo hydrolysis by traces of moisture with varying degrees of readiness. In this way, *cyclo*hexanoneoxime yielded N-cyclo*hexyl*cyclo*hexylideneketimine*,

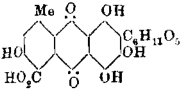
$$C_6H_{10}\!:\!N\cdot C_6H_{11},$$

b. p. 117—118°/9 mm., D_4^{27} 0·940, n_D^{27} 1·4972, giving a *hydrochloride*, m. p. 180° (decomp.). Acetophenoneoxime yielded *phenylmethylketimine*, CPhMe:NH, isolated as its *hydrochloride*. Propiophenoneoxime gave *phenylethylketimine*, yielding a *hydrochloride*, m. p. 145°, an *acetyl* derivative, m. p. 126°, and a condensation product, N-α-*phenylpropylphenylethylketimine*, CPhEt:N·CHEtPh, b. p. 170—171°/9 mm. Benzophenoneoxime yielded *diphenylketimine*, CPh_2:NH, and phenyl-α-naphthylketoxime gave *phenyl-α-naphthylketimine*, $C_{10}H_7$·CPh:NH, m. p. 68—69°. The imine group appears to become more stable with respect to water as the groups attached to it become more electronegative in character, the stability of the ketimines described above increasing in the order in which they are given.

W. G.

Carminic Acid. OTTO DIMROTH and HANS KÄMMERER (*Ber.* 1920, **53**, [*B*], 471—480).—It has been shown previously (A., 1913 i, 977) that carminic acid is a hydroxyanthraquinone, and the similarity of its absorption spectra and tinctorial properties to those of kermes dye (A., 1916, i, 561) points to the conclusion that it, like the latter, is a hydroxyanthrapurpurin. This is now shown to be the case. It is also found that complete acetylation of carminic acid yields an octa-acetyl derivative. Since, however only four hydroxyl groups are present in the anthraquinone nucleus, it follows that the remaining four must be present in the side-chain, to which the composition $C_6H_{13}O_5$ has been previously assigned. If, now, one oxygen atom of the latter is present in an ethereal, aldehydic, or ketonic form, a modification of the formula becomes essential, and the side-chain is now considered to be $C_6H_{11}O_5$, the alteration being found to give calculated values which agree with the observed analytical data as well as did those based on the older formula. The constitution of the side-chain has not been fully elucidated. It appears probable that it has a sugar-like structure, although carminic acid is certainly not a glucoside. It contains at least one asymmetric carbon atom, since carminic acid is now found to be optically active, and this phenomenon cannot be attributed to the structure of the nucleus, since kermesic

acid, and also the less closely related laccaic acid, are optically inactive. The structure of carminic acid, as far as it has been elucidated, is expressed by the annexed formula.



Under suitable conditions, carminic acid is reduced by zinc dust and glacial acetic acid to a leuco-compound, which is converted by atmospheric oxidation into *deoxycarminic acid*, yellowish-red needles, which is best purified by conversion into its *acetyl* derivative, orange-yellow needles, m. p. 245—250° (decomp.). The loss of a β-hydroxyl group during the reduction has its parallel in the cases of kermesic acid and hydroxyanthrapurpurin (Dimroth and Fick, A., 1916, i, 561), whilst the presence of two hydroxyl groups in the 1:4-position relative to one another in the reduction product is shown by its oxidation to a diquinone, from which carminic acid is regenerated by the action of acetic anhydride and sulphuric acid.

Octa-acetylcarminic acid is most conveniently prepared by the action of acetic anhydride and a little concentrated sulphuric acid on carminic acid at the ordinary temperature. When, however, carminic acid is warmed with acetic anhydride in the absence of a catalyst, a *hexa-acetyl* derivative, yellowish-red, cubic crystals, which soften and decompose at 170°, is smoothly formed; two hydroxyl groups in the α-positions on the nucleus remain unaffected, since the substance is readily converted by lead tetra-acetate into an unstable diquinone, which is reduced by sulphurous acid to the parent substance.

Carminic acid has $[\alpha]_{546}^{15}$ +51·6° in aqueous solution, whilst octa-acetylcarminic acid has $[\alpha]_{D}^{18}$ +80·55° in chloroform. Deoxycarminic acid is strongly active, but the acetyl derivatives of kermesic and laccaic acids are completely inactive. H. W.

The Acetylation of Hydroxyanthraquinones and Anthradiquinones. OTTO DIMROTH, OTTO FRIEDEMANN, and HANS KÄMMERER (*Ber.*, 1920, **53**, [*B*], 481—487).—In connexion with the observations made during the acetylation of carminic acid (preceding abstract), the authors have investigated the behaviour of various hydroxyanthraquinones when similarly treated, and find that, quite generally, the hydroxyl groups in the α-position are far less readily attacked than those in the β-position. A convenient method for the preparation of β-acetylated derivatives consists in allowing calculated quantities of acetic anhydride and the hydroxy-compound to react in cold pyridine solution; with an excess of anhydride, the α-hydroxy-groups are also attacked.

2-Hydroxyanthraquinone is completely acetylated when boiled for ten minutes with acetic anhydride, whilst, under similar conditions, 1-hydroxyanthraquinone is scarcely attacked; after six hours' treatment, however, the latter is largely acetylated. *Purpurin 2-acetate*, prepared from the components in hot pyridine solution, forms orange-coloured crystals, m. p. 172—173°, and is oxidised by lead peroxide or lead tetra-acetate to *2-acetylpurpurin-*

quinone, straw-yellow, slender needles, m. p. 167—168°. *Alizarin-bordeaux 2-acetate*, $C_6H_2(OH)_2<\begin{matrix}CO\cdot C\cdot C(OH):C\cdot OAc\\ CO\cdot \overset{\|}{C}\cdot C(OH):CH\end{matrix}$, forms red needles, m. p. 246—247°. *Hydroxyanthrapurpurin 2:7-diacetate* crystallises in orange-coloured needles, m. p. 224—225°, and is oxidised by lead tetra-acetate to an unstable diquinone, which was not obtained in the crystalline condition.

An improved process for the oxidation of quinizarin to 1:4:9:10-anthradiquinone, either by means of lead peroxide or lead tetra-acetate, has been worked out (compare Dimroth and Schultze, A., 1916, i, 563). In a similar manner, mono- and di-bromoquinizarin are oxidised to *3-bromo-1:4:9:10-anthradiquinone*, straw-yellow, flat needles, m. p. 212—214° (decomp.), and *2:3-dibromo-1:4:9:10-anthradiquinone*, yellowish-green, six-sided leaflets, which become red without melting at 300°, respectively.

Purpurinquinone 2-acetate is transformed by acetic anhydride and sulphuric acid into tetra-acetoxyanthraquinone, m. p. 205°, which is hydrolysed to 1:2:3:4-tetrahydroxyanthraquinone.

H. W.

Constituents of Indian Turpentine from Pinus longifolia, Roxb. I. JOHN LIONEL SIMONSEN (T., 1920, **117**, 570—578).

Hot Vulcanisation of Caoutchouc. F. KIRCHHOF (*Kolloid Zeitsch.*, 1920, **26**, 168—173).—A theoretical paper in which the author criticises the views of Harries (*Untersuch. natürlich. Künstlich. Kautschukarten*) (A., 1916, i, 659). The author claims that, previously to Harries, he had put forward the physico-chemical principles on which the hot vulcanisation of rubber takes place. Several experiments with lead oxide and lead sulphide mixed with small quantities of sulphur and a small quantity of sulphur-free organic catalyst are described, which show that vulcanisation can be effected with other substances than sulphur. In view of the advances in the knowledge of the constitution of rubber by the work of Harries, and the behaviour of depolymerised rubber on bromination (Schmitz, *Gummi Zeit.*, 1919, **34**, 1937), it is held that the chemical interpretation of the vulcanisation process is likely to undergo many modifications.

J. F. S.

Artemisin. P. BERTOLO (*Gazzetta*, 1920, **50**, i., 109—113).—The conclusions concerning the constitution of artemisin drawn from the author's previous investigations (A., 1904, i, 177; 1905, i, 224, 897; 1908, i, 560; 1911, i, 898) are briefly summarised. Short descriptions are now given of the products obtained by the action of various reagents on artemisin; the constitutions of these products are to be discussed later.

The action of dilute sulphuric acid (1:1) on artemisin at temperatures below 60° yields a white, crystalline compound, m. p. 236°, $[\alpha]_D$ −84·16°, insoluble in alkali carbonate solution, but soluble in alkali hydroxide solution, from which it is precipitated unaltered by means of carbon dioxide; in this compound, the

lactonic linking is preserved, but not the ketonic carbonyl, which appears to be converted into the phenolic group, C·OH, with formation of a desmotropo-artemisin. The action of more concentrated sulphuric acid at 100° gives a red oil, which solidifies on cooling and dissolves almost completely in alkali carbonate solutions, and appears to be identical with the dextrorotatory artemisic acid obtained by the action of hydrochloric acid on artemisin.

Treatment of artemisin with hydriodic acid and red phosphorus yields an acid compound, which somewhat resembles artemisic acid, but has the lower m. p. 98° and the higher specific rotation $[\alpha]_D + 72 \cdot 3°$. This compound forms white crystals, but gradually reddens and partly resinifies on exposure to light. It is also formed when artemisin is treated with iodine in alcoholic solution, and is probably a product of the further reduction of artemisic acid, from which it is apparently formed by reduction with sodium amalgam.

Acetic anhydride does not act on artemisin, but acetyl chloride converts it into the pale yellow *acetyl* compound, $C_{15}H_{17}O_4Ac$, m. p. 200°, $[\alpha]_D - 52 \cdot 60°$, which, when hydrolysed with potassium hydroxide, gives, not artemisin, but a moderately stable acid *compound*, m. p. 200°.

According to the conditions employed, the action of chlorine on artemisin yields one of three chloro-derivatives, m. p. 135°, 230°, and 180° respectively.

Reduction of artemisin by means of sodium amalgam gives, in almost theoretical yield, a crystalline, optically inactive, acid *compound*, m. p. 170°, the *barium* salt and *ethyl* ester of which have been analysed.

Exposure to light of a solution of artemisin in 50% acetic acid for about two months at a temperature never exceeding 35° results in the formation mainly of a white, crystalline *compound*, m. p. 242°, which exhibits lactonic and phenolic functions, and appears to be a new desmotropic form of artemisin. Exposure of the same solution to light during the summer months, when the temperature may sometimes reach 45°, yields principally a white *acid*, m. p. 168°.

Barium hydroxide on heating strongly attacks artemisin, giving ill-defined decomposition products; from the resinous substances obtained, an acid compound, m. p. 168°, which does not react with phenylhydrazine, was with difficulty isolated in an impure condition. T. H. P.

Action of Sulphuric Acid on Artemisin: *desmotropo-* **Artemisin.** P. BERTOLO (*Gazzetta*, 1920, **50**, i, 114—119. Compare preceding abstract).—l-desmotropo-*Artemisin*, $C_{15}H_{18}O_4$, prepared by the action of dilute sulphuric acid on artemisin at temperatures below 60°, forms white, flattened crystals, m. p. 236°, and, when treated with boiling solutions of alkali or alkaline-earth hydroxides, yields the corresponding salts of an unstable, monobasic hydroxy-acid; when the latter is liberated, it undergoes ready conversion into the original lactone. With sulphuric

acid and ferric chloride, *l-desmotropo*-artemisin gives neither th santonin nor the artemisin reaction, but remains undissolved an without coloration even in the hot.

In aqueous solution, the *barium* salt, $(C_{14}H_{19}O_3\cdot CO_2)_2Ba$, gives with silver nitrate, the flocculent *silver* salt, which turns brow in the light and decomposes with formation of a silver mirror i the hot; with copper sulphate, a bluish-white precipitate; wit lead acetate, a flocculent, white precipitate, somewhat soluble i excess of the reagent; with ferric chloride in the cold, no pr cipitate, whereas in the hot, a red, flocculent precipitate slowl forms.

Acetyl-l-desmotropo-artemisin, $C_{15}H_{17}O_3\cdot OAc$, forms aggregate of radiating, shining crystals, m. p. 154—155°, $[\alpha]_D$ −66·90°.

Zinc dust and acetic acid are without action on *l-desmotrop* artemisin, no acid analogous to the santonous acids being obtaine in this way. T. H. P.

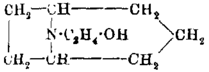
Rutin, the Flavone Pigment of Escholtzia californica, Cham CHARLES E. SANDO and H. H. BARTLETT (*J. Biol. Chem.*, 1920, **41** 495—501).—Nearly 5% of rutin is present in the petals o *Escholtzia californica*. It crystallises in fine, dense tufts of silk crystals, m. p. 190—192° (uncorr.). The accepted constitution o rutin (quercetin-glucoso-rhamnoside) is supported. Querceti m. p. 310°, glucosazone, and rhamnosazone were isolated after aci hydrolysis. J. C. D.

Solubilities of Theobromine. RAYMOND V. WADSWORT (*Analyst*, 1920, **45**, 133—134).—The recorded solubilities for theo bromine are inaccurate, the error apparently originating wit Mitscherlich, whose values for the solubility of the alkaloid i chloroform, ether, and water are much too high. The impurity t which this is to be attributed appears to have been caffeine. Th following amounts of pure theobromine were dissolved by differen solvents at 15·5° and at their boiling points respectively: ethyl ethe 0·003 and 0·003; benzene, 0·005 and 0·010; carbon tetrachlorid 0·020 and 0·040; chloroform, 0·060 and 0·070; boiling absolut alcohol, 0·100; water, 0·060 and 0·700; tetrachloroethane, 0·09 and 0·870; and aniline, 0·650 and 8·000%. C. A. M.

The Tropine and Cocaine Series. II. JULIUS VON BRAUN an KURT RÄTH (*Ber.*, 1920, **53**, [*B*], 601—614).—In continuation o previous work (von Braun and Müller, A., 1918, i, 233), the autho have further examined the influence of the relative positions o the hydroxyl group and the basic nitrogen atom and of the intro duction of double bonds on the physiological activity of th tropeines. Sufficient evidence has not, however, been collected t enable any general conclusion to be drawn with regard to mydriati action. The anæsthetic power, however, seems to attain its max mum when the hydroxyl group is in the γ-position to the nitroge atom, and, if this condition is fulfilled, to be independent of an

special mode of attachment of the hydroxyl group within the molecule. It is also increased by the introduction of double bonds into the seven-membered carbon ring.

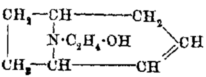
Tropane is most conveniently converted into nortropane according to the method of Willstätter and Iglauer, an elaboration of which is fully described. The latter is transformed by ethylene oxide into N-β-*hydroxyethylnortropine* (annexed formula), viscous oil, b. p. 127—128°/13 mm., which yields a *hydrochloride*, colourless, hygroscopic needles, m. p. 157°, a *platinichloride*, red needles, which decompose at 194—196°, a *picrate*, long, yellow needles, m. p. 181°, a *methiodide*, leaflets, m. p. 261°, and an oily *benzoyl* derivative (*hydrochloride*, m. p. 118°). Introduction of the tropic acid residue is effected in the manner previously adopted with mydriasin (*loc. cit.*); the substituted *amine*, however, is an oil, and yields a non-crystalline *hydrochloride*, *hydrobromide*, *oxalate*, *aurichloride*, and *platinichloride*. The *methiodide* forms colourless leaflets, m. p. 137—138°.



N-γ-*Hydroxypropylnortropane* is prepared in the form of its oily *benzoyl* derivative (*hydrochloride*, crystalline powder, m. p. 162°) by the action of γ-bromopropyl benzoate on nortropane; it is a colourless, moderately viscous liquid, b. p. 141—143°/22 mm., and forms a *picrate*, yellow needles, m. p. 121°, a *hydrochloride*, m. p. 155°, *platinichloride*, slender, yellow needles, m. p. 166°, and *methiodide*, m. p. 261°. N-p-*Nitrobenzoyl-γ-oxypropylnortropane*, m. p. 40° (*hydrochloride*, m. p. 236°; *picrate*, m. p. 186°), is prepared from the tropane and *p*-nitrobenzoyl chloride, and is reduced by stannous chloride to the *p*-aminobenzoyl *base*, which is an odourless, viscous oil (*dihydrochloride*, m. p. 215—216° after softening at 211°; *platinichloride*, m. p. 217° [decomp.]; *picrate*, m. p. 150°); the *acetyl* derivative could only be obtained as an oil, which gives a *picrate*, yellow, crystalline powder, m. p. 113°. The introduction of the new amino-group has very little effect on the physiological action of the base, probably since it does not markedly increase the already basic properties. γ-Hydroxypropylnortropane is converted into its *tropate* in the same manner as the corresponding β-derivative. Like the homologous tropeine, however, it is an oil, and yields oily salts; the *methiodide* is crystalline and has m. p. 111°.

N-ε-*Hydroxyamylnortropane* is obtained as an oily *benzoyl* derivative (*hydrochloride*, m. p. 181°; *platinichloride*, m. p. 176°; *picrate*, m. p. 112—113°) by the action of ε-bromoamyl benzoate on nortropane; it is a transparent, rather viscous liquid, b. p. 174—176°/20 mm., which yields a *picrate*, yellow leaflets, m. p. 97°, a *platinichloride*, yellow needles, m. p. 202°, and a crystalline *methiodide*, which does not melt below 270°. The corresponding *tropeine* is obtained by the aid of acetyltropyl chloride; it is an oil, which only yields oily derivatives.

N-β-*Hydroxyethylnortropidine* (annexed formula), colourless, rather viscous oil, b. p. 115—117°/12 mm., is prepared by the action of ethylene oxide on nortropidine in chloroform solution in the presence of a trace of water; it gives a *platinichloride*, long, yellow needles, m. p. 158°, a *picrate*, orange leaflets, m. p. 162°, and a coarsely crystalline *methiodide*, which does not melt below 270°. The *benzoyl* derivative is an oil, the *hydrochloride* of which has m. p. 184°. The *tropyl* derivative closely resembles that obtained from ε-hydroxyamylnortropane; the oily *methiodide* could, however, be converted into a crystalline *platinichloride*, $C_{38}H_{52}O_6N_2Cl_6Pt$, yellow, crystalline powder, m. p. 139° (decomp.), after darkening above 120°.



The *benzoyl* derivative of *N*-γ-hydroxypropylnortropidine, prepared from nortropidine and γ-bromopropyl benzoate, is a moderately viscous, non-crystallisable oil, which yields a *hydrochloride* m. p. 165—167°. It appears to be smoothly hydrolysed t‹ N-γ-*hydroxypropylnortropidine*, but lack of material prevented th‹ fuller investigation. H. W.

Triphenylpyridine, Acetophenonine, and Acetophenin‹ W. Dilthey and F. Kiefer (*Ber.*, 1920, **53**, [*B*], 621—622).—‹ has been shown recently by Reddelien (this vol., i, 316) th Engler's acetophenonine [described in the latest edition of B‹ stein's Handbuch as acetophenine] is identical with triphenylp‹ idine. This is confirmed by the authors, who have further prepa‹ the trinitrotriphenylpyridine described by Engler and Heine. L Reddelien, they find that the yields of triphenylpyridine obt‹ able from acetophenone and benzaldehyde or benzonitrile are v small, and consider the substance to be most conveniently ‹ pared by the action of ammonia on arylated pyrilium salts.

H. W

Formation of 4-Benzyl-3-methyl-5-pyrazolone. F‹ cesco Cherchi (*Gazzetta*, 1920, **50**, i, 120—127).—4-*Benz*‹ *methyl-5-pyrazolone*, $CO<\begin{matrix}NH\text{———}N \\ CH(CH_2Ph)\cdot CMe\end{matrix}$, obtained by the a‹ of hydrazine hydrate on methyl or ethyl α-benzylacetoaceta‹ aqueous-alcoholic solution, forms white needles, m. p. 228— When treated in alcoholic solution with sodium ethoxide, it ‹ the *sodium* salt, $C_{11}H_{11}ON_2Na$, and a *compound*, which cryst‹ in needles, m. p. 141—142°. The *picrate*, $C_{11}H_{12}ON_2,C_6H_3$‹ forms yellow needles, m. p. 154·5°. 1(?)-*Acetyl-4-ben*‹ *methyl-5-pyrazolone*, $C_{11}H_{11}ON_2Ac$, forms silky, white n‹ m. p. 128—129°.

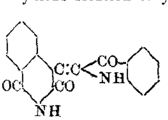
4-*Benzyl-3-methyl-1(?)-ethyl-5-pyrazolone*, $C_{11}H_{11}ON_2Et$, pared by the action of ethyl iodide on the pyrazolone dissol sodium ethoxide solution, crystallises in large, colourless ‹

m. p. 177°, and is accompanied by a yellow, oily compound, which is to be investigated later. T. H. P.

Dibutylbarbituric Acid. O. KAMM and E. H. VOLLWEILER (U.S. Pat. 1331712).—To the solution of 40 grams of sodium in 1000 c.c. of absolute alcohol are added 157 grams of ethyl dibutylmalonate (prepared by the interaction of butyl bromide and ethyl malonate in the presence of 2 mols. of sodium ethoxide) and 50 grams of carbamide, and the mixture is heated for six hours under pressure at 100—110°. The alcohol is then removed by distillation, water is added, and dibutylbarbituric acid, colourless needles, m. p. 158°, is precipitated by hydrochloric acid, the yield being 130 grams. The substance has pronounced sedative properties with but slight toxicity. CHEMICAL ABSTRACTS.

The Cyanine Dyes. I. The Constitution of the *iso*Cyanines. WILLIAM HOBSON MILLS and ROBERT SCOTT WISHART (T., 1920, **117**, 579—587).

Dyes Derived from 1 : 3-Dioxy*iso*quinoline [*o*-Homophthalimide]. W. HERZOG (*Ber.*, 1920, **53**, [*B*], 564—567).—Homophthalimide is readily condensed with α-isatinanilide in acetic anhydride solution to yield 1 : 3-*dioxy*-4-iso*quinoline*-2′-*indoleindigo* [1 : 3-*diketo*-4(2′)-*indoxyltetrahydro*iso*quinoline*] (annexed formula), reddish-violet, amorphous powder, m. p. about 270°, which is readily decomposed by dilute solutions of alkali hydroxides, but can be converted into its leuco-compound by zinc dust and acetic acid; it gives dark violet shades on wool. Similarly,



β-isatinanilide yields 1 : 3-*dioxy*-4-iso*quinoline*-3′-*indoleindigo* [1 : 3-*diketo*-4(3′)-*indoxyltetrahydro*iso*quinoline*], brown needles, m. p. about 300°, which is slowly decomposed by cold alkali hydroxide solutions. It can be reduced by hyposulphite in the presence of alkali or by zinc and acetic acid, but the vat is devoid of tinctorial properties. 1 : 3-*Dioxy*-4-iso*quinoline*-2′-*thionaphthenindigo* [1 : 3 : 3′-*Triketo*-4(2′)-*thionaphthentetrahydro*iso*quinoline*], from *o*-homophthalimide and thionaphthenquinoneanilide, crystallises in yellowish-red needles, m. p. about 250° (decomp.). The leuco-compound can be prepared in the usual manner, but has little affinity for the fibres, giving fugitive cherry-red shades on wool and pale pink tones on cotton. H. W.

The Stabilisation of Nitrous Acid in Connexion with Reactions carried out with this Compound; Applications to Diazotisation. E. BRINER and R. JONAS (*Helv. Chim. Acta*, 1920, **3**, 366—369).—The reversibility of the decomposition of nitrous acid into nitric acid, nitric oxide, and water suggests that solutions of the acid should be stable in presence of nitric oxide under pressure. This principle has been successfully applied to

the diazotisation of dinitroaniline, tribromoaniline, and *p*-sulphobenzeneazo-α-naphthylamine, which is difficult under ordinary conditions, by condensing nitrogen trioxide in a cooled tube containing the amino-compound and hydrochloric acid, sealing the tube, and allowing the temperature to rise. Picramide was not diazotised by this treatment. The value of the use of compressed air, proposed in the case of the last of the above three compounds (D.R.-P. 143450), is probably to be explained in the same way.

J. K.

Origin of the Humin formed by the Acid Hydrolysis of Proteins. V. ROSS AIKEN GORTNER and GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 821—827. Compare this vol., i, 400).—Pursuing their inquiry as to the nature of the reaction by which humin is produced, the authors prepared artificial mixtures of thirteen of the amino-acids commonly obtained by the hydrolysis of proteins. Such mixtures, when boiled for twenty-four hours with hydrochloric acid in presence of either trioxymethylene or tyrosine and trioxymethylene, or tryptophan and tyrosine, gave no insoluble humin; but this was produced when tryptophan, tyrosine, and formaldehyde were present. The reaction is therefore dependent on the presence of tryptophan, and can serve as a quantitative measure of the amount of this substance present. Similarly, soluble humin is derived from tyrosine, but, owing to its solubility, the amount is not a quantitative measure of the tyrosine. Phosphotungstic humin was produced to an equal extent in all the experiments, and may represent only an adsorption phenomenon. It is specially noted that the amino-group of cystine was not displaced in these experiments. J. K.

The Action of Thrombin on Fibrinogen. JOHN OGLETHORPE WAKELIN BARRATT (*Biochem. J.*, 1920, **14**, 189—209).—Fibrinogen in solution is diphasic, consisting of a concentrated phase which is dispersed, and a dilute phase which is continuous.

The action of thrombin is to form fibrin only from the fibrinogen in the concentrated phase, and is purely catalytic. A hypothesis of the mode of formation of fibrin fibrils is advanced. When fibrinogen in the concentrated phase is converted into fibrin, the equilibrium between the phases is disturbed, and more fibrinogen passes from the continuous to the disperse phase. This is then converted into fibrin. The "growth" of fibrin fibrils proceeds at a unimolecular rate. J. C. D.

The Mode of Union of Iron in the Prosthetic Group of Blood Pigments and the Constitution of Hæmin. WILLIAM KÜSTER (*Ber.*, 1920, **53**, [*B*], 623—633).—The communication is mainly devoted to a reasoned, adverse criticism of the views propounded by Willstätter (A., 1915, i, 289). The author maintains his ideas (A., 1912, i, 670) that two of the nitrogen atoms in hæmin are basic, and are so related to the two carboxyl groups that one nitrogen is united to one carboxyl group as

a betaine complex, leaving one carboxyl group, which alone can be easily esterified. In support of this hypothesis, it is now shown that the *diethyl ether* of *haematoporphyrin*, red, crystalline powder without a distinct melting point (the *silver* salt and the very hygroscopic *dihydrochloride* are described), is transformed by a boiling 1% solution of hydrogen chloride in ethyl alcohol into an isomeric *diethyl ether*, needles (and is thus not esterified), which is slowly converted by *N*-hydrochloric acid into the dihydrochloride of the original material; with more concentrated alcoholic hydrochloric acid solution, hæmatoporphyrin diethyl ether is converted into *tetraethylhaematoporphyrin*, steel-blue powder, m. p. about 91—93°. The action of diazomethane on hæmin has been investigated previously (A., 1918, i. 199), and this is now shown to differ fundamentally from its effect on the hydrochlorides of the triphenylmethane dyes, since, in the former class, the halogen atom is never removed, whilst in the latter series it is eliminated as methyl chloride, and the leuco-base is formed. It is therefore probable that the halogen atom is directly united to the iron atom, and this is rendered more probable, since measurement of the electrolytic conductivity of hæmin and its dimethyl ester in pyridine solution shows them to behave in the same manner as inorganic salts. H. W.

Refractivity of Hæmoglobin in Solution. FREDERICK H. HOWARD (*J. Biol. Chem.*, 1920, **41**, 537—547).—The refractive index of hæmoglobin solutions varies directly with concentration and is independent of the presence of other proteins, and of bases and salts in low concentration. The value of *a* for hæmoglobin is 0·00183. J. C. D.

Hæmocyanin. III. CH. DHÉRÉ (*J. Physiol. Path. gén.*, 1919, **18**, 503—526; from *Physiol. Abstr.*, 1920, **5**, 7).—Hæmocyanin of the snail can be obtained in a crystalline form by dialysis against distilled water, by exposing the blood to a potential difference of 120 volts after dialysis, or cooling the supernatant liquid in the dialyser in ice. It may be purified by solution in a very small amount of *N*/500-sodium sulphate, from which it crystallises on cooling in ice. Hæmocyanin of the rock lobster can be crystallised by the last method, and that of cephalopods by the method of Hopkins and Pinkus, using concentrated ammonium sulphate. The varying forms of crystals obtained are probably due to differences in the proportions of water of imbibition, not of hydration.

W. G.

Properties of the Nucleotides obtained from Yeast Nucleic Acid. P. A. LEVENE (*J. Biol. Chem.*, 1920, **41**, 483—493).—The work reported in this paper was carried out in order to clear up the discrepancies in the reported properties of the nucleotides from yeast.

Adenosinephosphoric acid, $C_{10}H_{14}O_7N_5P,H_2O$, is the most insoluble of the four nucleotides. It decomposes with effervescence at 195°

(corr.); $[\alpha]_D^{50}$ −40·5° in 1% aqueous solution, −40·5° to −44·5° in 5% aqueous-ammonia solution; $[\alpha]_D^{20}$ −38·0° in 10% hydrochloric acid, −59·5° in 2% sodium hydroxide, −66·0° in 5% sodium hydroxide.

Guanosinephosphoric acid, $C_{10}H_{14}O_8N_5P,2H_2O$, *contracts on heating* at 175° (corr.) and decomposes at 180°. $[\alpha]_D^{25}$ −7·5° in water, +1·5° in 10% hydrochloric acid; $[\alpha]_D^{20}$ −44·0° in 5% aqueous ammonia; $[\alpha]_D^{25}$ −57·0° in 2% aqueous sodium hydroxide, −65·0° in 5% aqueous sodium hydroxide.

Cytidinephosphoric acid, $C_9H_{14}O_8N_3P$, prisms, decomp. 230—233° (corr.), slow heating. $[\alpha]_D^{50}$ +40·0° to +48·5° in water; $[\alpha]_D^{25}$ +26·0° in 10% hydrochloric acid, +44·5° in 5% ammonia, +25·5° in 2% sodium hydroxide; $[\alpha]_D^{20}$ +1·0° and −21·0°, respectively, in 5 and 10% sodium hydroxide.

Uridinephosphoric acid, $C_9H_{13}O_9N_2P$, small bunches of needles. m. p. 198·5° (corr.; decomp.). $[\alpha]_D^{20}$ +9·5° in water, +6·5° in 2% sodium hydroxide, and −15·0° in 5% sodium hydroxide.

Monoammonium salt of uridinephosphoric acid, fine, curved, felted needles, *decomp.* 240°. $[\alpha]_D^{50}$ +10·5° in water; $[\alpha]_D^{25}$ +2·5° in 10% hydrochloric acid, +14·0° in 5% ammonia; $[\alpha]_D^{20}$ +1·5°, −16·0°, −26·0°, respectively, in 2, 5, and 10% sodium hydroxide.

Adenosine has $[\alpha]_D^{20}$ −60·0° in aqueous solution, −43·5° in 10% hydrochloric acid, −68·5° in 5% sodium hydroxide.

Uridine, $[\alpha]_D^{20}$ +4·0° in water, +5·0° in 10% hydrochloric acid. −6·0° in 5% sodium hydroxide.

The changes in the optical rotation are probably due to several causes, amongst which tautomeric changes possibly play an important part. Adenosine and uridine show the same character of optical rotation as the corresponding nucleotides. J. C. D.

The Theory of Gels. II. The Crystallisation of Gelatin. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1920, **14**, 91—93).—It has been previously shown (A., 1919, ii, 139) that the reversible gelation of the natural emulsoids is a crystallisation process resulting from the viscosity of these substances and from their very small diffusion constants, which greatly retard the crystallisation of the cooling sols, altering the accumulation of a large excess concentration. Hydrosols of "crystal" leaf gelatin of 0·5 and 0·3% were made, quickly heated to 100°, and filtered into thoroughly clean, covered crystallising dishes. A small amount of mercuric chloride was added to prevent bacterial growth, and the solutions were allowed to evaporate at the ordinary temperature. By this means, a precipitate, consisting of microscopic spherites 0·25 μ to 0·28 μ in diameter, was obtained. From these results, it cannot be doubted that gelatin crystallises from water exactly as indicated by von Weimarn's theory. J. C. D.

***Swelling of Gelatin in Hydrochloric Acid and Sodium* Hydroxide.** DOROTHY JORDAN LLOYD (*Biochem. J.*, 1920, **14**, 147—170).—This paper furnishes further experimental support to

the theory which holds that gelatin is an amphoteric colloid, the neutral form of which is stable only at the isoelectric point (P_H 4·6, 20°). The molecular weight is 10,000 or some multiple of 10,000. This neutral gelatin is only slightly soluble in hot water, and is insoluble in cold water. It may, however, combine with water to form complexes, perhaps of the nature of hydrates or solid solutions. On the acid side of P_H 4·6, gelatin functions as a multi-acid base, giving rise to ionisable hydrochlorides, and at P_H 2·5 practically all the protein exists in the form of such salt. At lower hydrogen-ion concentrations than that of the isoelectric point, gelatin acts as a polybasic acid, forming ionisable gelatinates with bases such as sodium. The reaction with hydrochloric acid is reversible, that with sodium hydroxide irreversible. The formation of keto-salts in acids and enol salts in alkalis is postulated.

Regarding gels, the author is of the opinion that they are two-phase structures consisting of a solid framework of precipitated neutral gelatin, with which is combined a certain amount of water, and an interstitial fluid which is a solution of gelatin salt. The volume of any system in the gel condition is determined by two opposing sets of forces, the elastic forces of the solid framework, which tend to make the volume contract, and the osmotic forces of the ionised gelatin salts dissolved in the interstitial fluid, which tend to make the volume expand. Hence neutral gelatin, being only one phase, cannot make a stable gel, but will make a gel which will be free to contract. Similarly, since the salt form of gelatin is a single phase, such cannot form a gel. Gelatin in this form will only form sols with water.

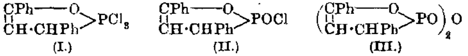
The volume occupied by a gelatin gel swelling in a fluid medium depends on the ratio of the mass of the dissolved electrolyte to the mass of gelatin, on the geometrical form of the gel, and also on the hydrogen-ion concentration of the medium. Gels which are swelling in a weakly acid or alkaline medium lose water on being transferred to an atmosphere of saturated vapour. The amount of water lost is a function of the reaction of the previous external fluid. This loss follows from the elastic properties of the gel, and is shown to be in accordance with the membrane theory of Donnan. Van Bemmelen's theory that the surface of a gel is to be regarded as a solid membrane perforated by pores is confirmed by observation. J. C. D.

Chemical Kinetics of Catalase. I. Catalase from Phyl. mit., Riv. EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 13—58. Compare this vol., i, 194).—The velocity of decomposition of hydrogen peroxide by means of the catalase from *Phyllostachys mitis*, Riv., has been investigated at 0°, 10°, 12·5°, 18°, and 25°. The catalase is obtained by crushing an edible sprout from a species of bamboo with water saturated with toluene. It was observed that the activity of the catalase steadily decreased during the reaction. The velocity of the reaction is represented by the equations $-dC/dt=kEC$ and $-dE/dt=-k'/k.dC/dt=k'EC$, where E and C are the concentration of the enzyme and

hydrogen peroxide respectively, and k and k' the reaction constants. *The decrease of activity of the catalase is caused by the substrate* and the product of the reaction, and its rate is approximately proportional to the principal reaction. The decrease of activity cannot be attributed to the change of the concentration of hydrogen ions produced by the decomposition of hydrogen peroxide, because a similar decrease of activity also occurs in acid solutions where the hydrogen-ion concentration is constant. The relative activity *of the enzyme is always proportional to its concentration if the* concentration of the hydrogen ion is maintained throughout the experiment. In a very dilute solution of hydrogen peroxide and a relatively concentrated solution of the enzyme, the activity increases in the first stage and then decreases. This may probably be explained by the following: (i) The ordinary reaction would be carried out at a rate somewhat higher than that calculated for *a first-order reaction. (ii) The rate is decreased by oxygen and* hydrogen peroxide in ordinary cases. (iii) Such effects are observed only in the course of reactions in very dilute solutions, because the concentrations of both the substrate and the product are very small, that is, the velocity constant has a maximum value. (iv) The retardation occurs with a measurable velocity, which is approximately proportional to the principal reaction. This explanation is *in keeping with the observations of Waentig and Steche* (A., 1913, i, 304) for solutions which were rapidly stirred in a vacuum.

J. F. S.

A New Type of Addition Reaction. JAMES B. CONANT and ALAN A. COOK (*J. Amer. Chem. Soc.*, 1920, **42**, 830—840. Compare A., 1918, i, 74).—The formation of ketophosphinic acids by the interaction of $\alpha\beta$-unsaturated ketones and phosphorus trichloride in presence of acetic acid is complete before the addition of water to the mixture, since the acid may be precipitated by the addition of benzene; acetyl chloride is the other product of the reaction. The first stage in the reaction with phenyl styryl ketone probably consists in the formation of the compound (I), since if acetic anhydride be used at the ordinary temperature in place of acetic acid, a mixture is produced of the acid chloride (II), a light-coloured, viscid oil, with an amount of the anhydride (III) which increases with the quantity of acetic anhydride employed. Water readily converts these compounds into β-benzoyl-α-phenylethyl-



(I.) (II.) (III.)

phosphinic acid, and they combine with bromine to give products, from which, by decomposition with water, *β-bromo-β-benzoyl-α-phenylethylphosphinic acid*, COPh·CHBr·CHPh·PO(OH)$_2$, m. p. 196°, is produced. This compound may also be prepared by bromination of β-benzoyl-α-phenylethylphosphinic acid. It is at once converted by sodium hydrogen carbonate, sodium carbonate, or sodium hydroxide into phenyl styryl ketone, sodium bromide,

and sodium phosphate. Its *monophenyl* ester, m. p. 179°, was produced by the action of phenol on the crude chloride obtained by treating with thionyl chloride either the acid or the product of the condensation of phenyl α-bromostyryl ketone with phosphorus trichloride and acetic acid; it is best prepared by brominating *phenyl β-benzoyl-α-phenylethylphosphinate*, m. p. 146°, which is obtained from the corresponding acid through the chloride. *Diphenyl β-benzoyl-α-phenylethylphosphinate*, m. p. 125°, results in small quantities in the preparation of the monophenyl ester, but is best obtained by treating the acid with two molecular proportions of thionyl chloride, and subsequently with phenol. It dissolves in cold sodium ethoxide solution, and is converted into the monophenyl ester. The monophenyl ester is also obtained by treating the mixture of the compounds (II) and (III) with phenol. It is accompanied by the compound, $\begin{matrix}CPh\text{——}O\\ \| \\ CH\cdot CHPh\end{matrix}\!\!>\!PO\cdot OPh$, an oil insoluble in cold aqueous alkali, but convertible into the monophenyl ester either by solution in alcoholic sodium hydroxide solution or by treatment first with hydrogen chloride at 125° and then with water.

J. K.

Improved Method for the Preparation of Primary Arsanilic Acid. Harold C. Cheetham and John H. Schmidt (*J. Amer. Chem. Soc.*, 1920, **42**, 828—829).—Fichter and Elkind's process for the preparation of arsanilic acid (A., 1916, i, 444) gives only a fair yield, but better than that of Kober (A., 1919, i, 182). It was found best to heat a mixture of dry arsenic acid ($\frac{1}{4}$ gram-mol.) with aniline ($\frac{5}{3}$ gram.-mol.) for twelve hours at 150—160°, the yield of purified product being 26%. J. K.

Aromatic Mercuridicarboxylic Esters. Walter Schoeller, Walter Schrauth, and Richard Hueter (*Ber.*, 1920, **53**, [*B*], 634—643).—*The non-toxicity of mercuridipropionic acid* and mercuridibenzoic acid in comparison with the highly toxic mercury diaryls or dialkyls has been shown by Müller, Schrauth, and Schoeller (A., 1911, ii, 755) to be attributable to the excretion of the former unchanged from the organism in which the latter are decomposed. The present investigation deals with the production of mercuridicarboxylic acids, which would be more readily decomposed, and of their derivatives, which would not be eliminated, the ultimate object being an examination of their toxicity, the results of which are described elsewhere.

Methyl o-chloromercuribenzoate, $HgCl\cdot C_6H_4\cdot CO_2Me$, needles, m. p. 162° after softening at 142°, is prepared by heating methyl benzoate, mercury acetate, and glacial acetic acid, separation of the methyl di- and mono-o-acetoxymercuribenzoates by means of acetone, and treatment of a solution of the latter in aqueous alcohol with sodium chloride solution. It is converted by hydrogen

sulphide in methyl-alcoholic solution into *methyl sulphidodimercuri-o-benzoate*, $S(Hg\cdot C_6H_4\cdot CO_2Me)_2$, white, amorphous powder, which softens and gradually darkens when heated; the latter is transformed at 120° into *methyl mercuridi-o-benzoate*, colourless crystals, which is hydrolysed by *N*-sodium hydroxide solution to mercuridibenzoic acid, identical with the product prepared by Pesci in another manner.

Methyl acetoxymercurisalicylate, m. p. 202° (corr.) after slight previous softening, and *methyl* m-*chloromercurisalicylate*,

$$HgCl\cdot C_6H_3(OH)\cdot CO_2Me,$$

are prepared in the same manner as the corresponding benzoates, and are similarly transformed into *methyl sulphidodimercurisalicylate*, white, amorphous powder, and *methyl mercuridisalicylate*, m. p. 178—180° (corr.). *Ethyl acetoxymercurisalicylate*, needles, grouped in clusters, m. p. 206° (corr.) after softening at 200°, is converted by saturated aqueous sodium thiosulphate solution into *ethyl mercuridisalicylate*, m. p. 193° (corr.).

Methyl mercuridianthranilate forms small, yellow needles, m. p. 196—197° (corr.) after slight previous decoloration, whilst *methyl mercuridi-p-aminobenzoate* crystallises in yellow needles, m. p. 176° (corr.). H. W.

Phenylthiolmercuri-chloride. H. LECHER (*Ber.*, 1920, **53**, [*B*], 568—577).—In continuation of previous investigations (A., 1916, i, 41), the author has endeavoured to prepare a mixed mercaptide of the type $R'S\cdot Hg\cdot SR''$, and, for this purpose, has studied the action of phenylthiolmercuri-chloride, $HgCl\cdot SPh$, on sodium ethyl sulphide; reaction is found to proceed, for the greater part at any rate, in accordance with the equation $2HgCl\cdot SPh + 2NaSEt = 2NaCl + Hg(SPh)_2 + Hg(SEt)_2$, although the complete absence of the mixed mercaptide is not definitely proved. The possibility that the chloride should be formulated $Hg(SPh)_2,HgCl_2$ appeared to be discounted by determinations of the molecular weight in boiling ethyl acetate solution, which indicated the simple structure. The explanation of the course of the reaction is found in the observation that phenylthiolmercuri-chloride is dissociated in solution into mercury phenylmercaptide and mercuri-chloride, $2HgCl\cdot SPh \rightleftharpoons Hg(SPh)_2 + HgCl_2$. The chloride can be readily prepared by mixing solutions of equivalent amounts of mercury phenylmercaptide and mercuric chloride, and the latter can also be extracted from solutions of the mercurichloride in organic solvents by sodium chloride solution. Further, if a solution of phenylthiolmercuri-chloride in pyridine is treated with ammonia, mercuric chloride is precipitated, whilst mercury phenylmercaptide remains in solution.

Mercury phenylmercaptide has been shown to undergo partial dissociation when heated into phenyl disulphide and mercury (*loc. cit.*). It is now shown that phenylthiolmercuri-chloride behaves in an analogous manner; when heated, it exhibits thermochromism, and melts at 191·5°, dissociating for the greater part

into diphenyl disulphide and mercurous chloride. A small portion, however, always remains on decomposition, and, conversely, small amounts of phenylthiolmercuri-chloride can be obtained by heating a mixture of the disulphide and mercurous chloride. H. W.

Physiological Chemistry.

Variations in the Chemical Composition of Human Blood. FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1920, **41**, 599—615).—Whilst the total nitrogen, non-protein nitrogen, and sugar of the blood vary in the same person from week to week, there is a tendency for the level of these variations to be characteristically individual. There is no practical difference between the absolute amounts of the constituents in bloods taken fourteen hours after food and three and a-half hours after breakfast. The absolute amount of creatinine is constant for the individual and for the species. The variations of urea, uric acid, creatine, and other non-protein nitrogenous substances are discussed. J. C. D.

Anti-coagulating and Hæmolysing Action of Sodium Nucleate. Action on Brewer's Yeast. DOYON (*Compt. rend.*, 1920, **170**, 966—967).—Sodium nucleate used in the form of a powder possesses an anti-coagulating power and exerts a very energetic hæmolysing action. It also prevents the decomposition of sugar into alcohol and carbon dioxide by brewer's yeast. W. G.

Effect of Alkali Fluorides on Digestion. GROSSERON (*Ann. Chim. anal.*, 1920, [ii], **2**, 111).—According to some investigators, sodium fluoride has no action on the ordinary digestive process, but inhibits lactic, butyric, and acetic fermentation. It is suggested that the use of the salt as a preservative for butter should be permitted. W. P. S.

Effect of Intravenous Injections of Active Deposit of Radium on Metabolism in the Dog. RUTH C. THEIS and HALSEY J. BAGG (*J. Biol. Chem.*, 1920, **41**, 525—535).—The injection was followed by an increased excretion of nitrogen, which reached a maximum figure on the second day after treatment. Urea fluctuated with total nitrogen, but there was a definite increase in excretion of ammonia and uric acid. J. C. D.

Nutritive Factors in Plant Tissues. IV. Fat-soluble Vitamine. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1920, **41**, 549—565).—Rats

which received 0·1 gram of butter daily showed considerable ability to grow, whilst 0·5 gram per day is sufficient to restore to good nutritive condition and growth rats declining on diets deficient in the fat-soluble accessory substance. In comparison with these values, it is shown that 0·1 gram of dried tomato daily will supply all the fat-soluble factor for normal growth. Of other vegetables tested, cabbage was the least satisfactory, whereas 0·1 gram of dried lucerne, clover, timothy grass, and spinach will furnish at least as much of the vitamine as the same weight of butter.

The thermostability of the fat-soluble growth factor is discussed, and the observations of Steenbock, Boutwell, and Kent (A., 1918, i, 513) and of Drummond are not confirmed (A., 1919, i, 363).

J. C. D.

Relation between the Total Acidity, the Concentration of the Hydrogen Ion, and the Taste of Acid Solutions. R. B. HARVEY (*J. Amer. Chem. Soc.*, 1920, **42**, 712—714).—The sourness of fruit and fruit juices is shown to depend both on the hydrogen-ion concentration and on the total free acid contained in the juice. The tendency to produce hyperacidity in the ingestion of fruits is dependent on the total quantity of acid ingested, and not necessarily on the hydrogen-ion concentration alone. The addition of sugar does not affect this tendency, which, although it changes the taste, does not affect either the total acidity or the hydrogen-ion concentration. J. F. S.

The Formation of Ferrous Sulphide in Eggs during Cooking. CHARLES KENNETH TINKLER and MARION CROSSLAND SOAR. (*Biochem. J.*, 1920, **14**, 114—119).—The discoloration on the surface of the yolk of a "hard-boiled" egg is due to the formation of ferrous sulphide, by the liberation of hydrogen sulphide from the decomposition of a sulphur compound of the egg-white and its action on the iron contained in the yolk. J. C. D.

A Pressor Compound from the Pituitary Gland. ALBERT C. CRAWFORD (*J. Pharm. and Expt. Ther.*, 1920, **15**, 81—94).—The paper opens with a review of the literature on the active principles of the pituitary gland. The pressor substance is not extracted from the dried, powdered posterior lobes by alcohol, but is extracted by acidified alcohol. From this extract, anhydrous ether precipitates the compound as a white or slightly coloured amorphous product, which is readily soluble in water.

The fractionation of extracts prepared from the posterior lobes is described, and the preparation of a highly active pressor substance, which is precipitated by soluble mercury and silver salts, is described. No crystalline derivatives have yet been obtained.

J. C. D.

Zinc in the Human Organism. SINICHA GIAYA (*Compt. rend.*, 1920, **170**, 906—909).—The examination of the viscera of a number of corpses shows the invariable presence of zinc, the proportion

increasing with age. Thus, the amounts found varied from 0·0009% in the case of a child three months old up to 0·005% in the case of a man seventy years old. The distribution of zinc in the different organs corresponds with the following descending order: brain, lungs, stomach, liver, kidneys, intestine, heart, and spleen. W. G.

A Case of Adipocere. G. Florence (*Bull. Soc. chim. biol.*, 1919, **1**, 185—188).—A sample of adipocere gave negative tests for calcium. After removal of the fatty substances by extraction with ether, the residue contained 11·3% of nitrogen, and gave no reaction with Millon's reagent or Hopkins and Cole's reagent. It is therefore thought to be of the nature of collagen, which had escaped the transformation into fat. The author discusses the possibility of straight-chain polypeptides being converted into fatty acids, such as stearic acid, by a process of deaminisation and reduction.

J. C. D.

Milk as a Source of Water-soluble Vitamine. II. Thomas B. Osborne and Lafayette B. Mendel [with Alfred J. Wakeman] (*J. Biol. Chem.*, 1920, **41**, 515—523).—The authors have been unable to confirm in detail the classical experiments of Hopkins (A., 1912, ii, 779). They find that a much larger quantity of milk than the 2 c.c. used by Hopkins is necessary to supply the vitamines required by the rat for normal growth. The discrepancy does not appear to be due to the diet of the cow from which the milk is obtained, or to the character of the inorganic constituents of the artificial ration. J. C. D.

The Presence of Amylase in Milk and Cheese. Masayoshi Sato (*Biochem. J.*, 1920, **14**, 120—130).—The presence of amylase in milk, already reported by many workers, is confirmed. It is also present in commercial Cheddar cheese, although in variable amounts. Certain differences in the digestibility of various forms of starch by amylase were noted. J. C. D.

Acidosis. XVI. The Titration of Organic Acids in Urine. Donald D. Van Slyke and W. W. Palmer (*J. Biol. Chem.*, 1920, **41**, 567—585).—The organic acids present, both free and as salts, in urine are estimated by titrating between the hydrogen-ion concentrations represented by p_H 8 and p_H 2·7 respectively, after removal of phosphates and carbonates by means of calcium hydroxide. It appears that such titration represents between 95 and 100% of the organic acids present. It also includes weak bases, the dissociation constants of which fall within a range in the neighbourhood of 10^{-11}, but of this class only creatinine, and at times creatine, appear to be present in significant amounts in human urine. The average twenty-four-hour excretion of organic acids in normal young men appears to be about 5·7 to 9·8 c.c. of $0·1N$-acid (uncorrected for creatinine). There appears to be little difference in the rate of excretion during day and night.

Data from cases of methyl alcohol poisoning and diabetes are examples of acidosis due to organic acids of different types. In the first case, a part of the total organic acid excretion was due to formic, lactic, and hydroxybutyric acids, but the greater part to acids of unknown nature. In diabetes, the rise in the excretion of acetone substances is so accurately paralleled by the rise in titrated organic acids that it is probable (1) that organic acids other than the acetone substances are not excreted in significant amounts in diabetic acidosis, and (2) that the easily performed organic acid titration may be used for approximate estimation of the acetone substances in diabetic urine. J. C. D.

The Anti-scorbutic Properties of Concentrated Fruit Juices. III. ARTHUR HARDEN and ROBERT ROBISON (*Biochem. J.*, 1920, **14**, 171—177).—The anti-scorbutic property of orange juice is not appreciably destroyed by evaporation to dryness under suitable conditions.

The dry residue retains considerable activity after storage for two years in a dry atmosphere at the ordinary temperature. J. C. D.

Effect of Heat on the Anti-scorbutic Accessory Factor of Vegetable and Fruit Juices. ELLEN MARION DELF (*Biochem. J.*, 1920, **14**, 211—228).—When cabbage, swede, and orange juices are subjected to temperatures up to 130°, a corresponding reduction of their anti-scorbutic properties occurs. The destrnction is most marked in the case of cabbage juice, and least in the case of orange juice. The greater stability of orange juice to heat is maintained even when the juice is nearly neutralised before heating. There is evidence that growth may be affected by the limitation of the anti-scorbutic element in the diet, apart from the appearance of definite symptoms of scurvy and apart from deficiency in the other growth-promoting accessory factors.

The unexpected stability of swede and orange juice at temperatures above 100°, when the heating is conducted in the absence of air, may perhaps indicate that destruction of the anti-scorbutic factor is an oxidation process. This observation naturally has an important bearing on the canning and preserving of fruits and vegetables. J. C. D.

Physiological Action of Fumes of Iodine. A. B. LUCKHARDT, F. C. KOCH, W. F. SCHROEDER, and A. H. WEILAND (*J. Pharm. Expt. Ther.*, 1920, **15**, 1—21).—Iodine fumes may be absorbed from the human skin and appear in the urine. Iodine absorbed in this manner may actually increase the iodine content of the thyroid gland and induce a pronounced change in the histological features of that gland. The inhalation of small quantities of iodine fumes produces similar results, but larger doses may lead to respiratory disturbances and fatal acute pulmonary œdema. The administration of iodine by such inhalation is regarded as a dangerous procedure. J. C. D.

The Formation of Acetone Substances following Ether ιæsthesia and their Relation to the Plasma Bicarbonate. MES J. SHORT (*J. Biol. Chem.*, 1920, **41**, 503—513).—A study the acetoacetic acid, acetone, and β-hydroxybutyric acid of the ɔod was made before and after ether anæsthesia in order to ːertain whether the formation of these substances was in any ·y responsible for the fall in alkaline reserve which accompanies ıt condition. Apparently the so-called acetone substances are t formed promptly enough during ether anæsthesia to account · the decrease in plasma bicarbonate. The analytical methods · the acetone substances (Van Slyke and Fitz, A., 1919, ii, 436) ıy be rendered less accurate by the presence of fat and ether, or ıer alone. J. C. D.

The Minimum Concentration of ββ'-Dichloroethyl ılphide (Mustard Gas) Effective for the Eyes of Man. I. REED (*J. Pharm. Expt. Ther.*, 1920, **15**, 77—80).—Concen-.tions of 0·0005 mg. per litre of mustard gas will produce visible ıctions in less than one hour of exposure in the eyes of individuals ose cutaneous resistance is relatively high. J. C. D.

ıemistry of Vegetable Physiology and Agriculture.

Action of Bacillus fluorescens liquefaciens (Flügge) on rtain Amino-acids. A. BLANCHETIÈRE (*Bull. Soc. chim. biol.*, 20, **2**, 29—36. Compare A., 1916, i, 699).—The amino-acids are le to act as the sole source of carbon and nitrogen for the develop-ːnt of this organism. The rates and degree of attack are very riable, histidine, alanine, and asparagine being particularly suit-le for utilisation. Substitution of an amino-group by benzoyla-·n appears to oppose the utilisation of the amino-acid, an observa-·n which is in agreement with the accepted theories on the decom-sition of amino-acids by bacteria. The benzoyl derivatives are composed. J. C. D.

Influence of Reaction on Colour Changes in Tyrosine ılutions. (MRS.) ELFRIDA CONSTANCE VICTORIA VENN (*Biochem. J.*, 20, **14**, 98—102).—Cornish and Williams showed (A., 1917, i, 613) at certain groups of bacteria isolated from discoloured Stilton eeses are capable of producing changes of colour in media con-ːning suspensions of caseinogen and certain amino-acids. It was ınd that the reaction of the media on which the organisms were ɔwn exercised a powerful influence on the degree of discolora-·n. It is now shown that there is a definite range of reaction er which the organism studied is capable of producing a dis-

coloration in tyrosine solutions. A modified form of hydrogen electrode is described, which presents several advantages over many types now in use. J. C. D.

Comparative Studies on Respiration. X. Toxic and Antagonistic Effects of Magnesium in Relation to the Respiration of Bacillus subtilis. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1920, **2**, 331—336).—Magnesium chloride in concentrations below 0·01*M* has little effect on the rate of respiration of *B. subtilis*; at 0·03*M* there is an increase in the rate, whilst in the higher concentrations there is a gradual decrease. There is a marked antagonism between magnesium and sodium chlorides, and a very slight antagonism between the chlorides of magnesium and calcium. J. C. D.

The Fats of Tubercle Bacilli. H. AGULHON and A. FROUIN (*Bull. Soc. chim. biol.*, 1919, **1**, 176—184).—Large amounts of fatty substances may be extracted from dried tubercle bacilli by alcohol. This material is composed of fatty acids, neutral fats, esters of the higher alcohols, hydrocarbons, and a substance containing phosphorus. The latter represents about 14% of the total alcoholic extract of the organisms, and is composed of a mixture of substances of phosphatide character, which on hydrolysis yields fatty acids, glycerol, a base analogous to choline, and a gummy substance which yields dextrose. The presence of cholesterol in the extracts of the bacilli was not established. J. C. D.

Production of Formic Acid by Yeasts in Media containing Amides. P. THOMAS (*Ann. Inst. Pasteur*, 1920, **34**, 162—176. Compare this vol., i, 126).—The volatile acidity produced during the culture of yeast on media containing acetamide is in part due to the formation of formic acid and in part due to the formation of acetic acid, the relative proportions of these two acids varying with the conditions. The presence, in addition, of various ammonium salts has a very marked effect on the total volatile acidity and the relative amounts of the two acids produced. In the presence of ammonium sulphate, oxalate, succinate or hydrogen carbonate the volatile acid produced is almost entirely formic acid, whilst in the presence of ammonium aspartate the two acids are produced in almost equal amounts.

The author discusses the various theories put forward to explain the formation of acetic acid, and concludes that the mechanism is not a simple one, but that there are several phenomena, which will function according to the conditions and may replace or superpose on one another, as the conditions vary. W. G.

Alteration in the Inverting Power of Top Yeast by Pre-treatment. STURE LÖVGREN (*Fermentforsch.*, 1920, **3**, 221—240; from *Chem. Zentr.*, 1920, i, 473—474).—The experiments were undertaken with the object of determining the influence of the inorganic constituents on the formation of saccharase and

the differences between their action on bottom yeast, which has generally been used previously by Euler and his co-workers, and on top yeast. Pre-treatment of the yeast was effected with sugar, ammonium acetate, magnesium chloride or sulphate, calcium chloride, potassium chloride, sodium chloride, potassium dihydrogen phosphate, yeast water, alcohol, acetone, or carbamide, sometimes singly and sometimes in combinations. The results are summarised in the following statements: (1) The neutral salts investigated do not appear to have any actual influence on the variation of the inverting power of the types of top yeast used, either in small amounts at the ordinary temperature or in larger quantities at the ordinary or higher temperature. (2) Certain experiments indicate that the inverting power of top yeast may be distinctly increased by suitable pre-treatment. Addition of nitrogenous nutriment is advantageous, but not essential. In the first twenty-four hours (of fermentation) the inverting power increases slowly or may even decrease; after cessation of fermentation, it increases gradually at first, then more rapidly to a maximum, at which it remains for a time, and then slowly decreases again. The curves are more or less flattened according to the properties of the original yeast. (3) One experiment shows that top yeast is much less suitable for enrichment experiments of this kind than bottom yeast. (4) The inversion constants of the original yeasts varied between 20 and 40, with a mean value (from nine estimations) of 28 per gram of yeast (30% dry substance) and 9·6 grams of sucrose at 16°, from which the constant 3×10^{-12} is calculated. (5) If the increase of inverting power is considered to be a consequence of augmented vitality due to the pre-treatment, the nitrogen nutriment must be regarded as essential. The fact that a marked increase can occur without administration of nitrogen is probably explained by the formation of the necessary amount of the latter by autolysis. H. W.

Activation of Living Yeast by Yeast Extract and by Salts of Organic Acids. Hans von Euler (*Zeitsch. techn. Biol.*, 1919, **7**, 155—164; from *Chem. Zentr.*, 1920, i, 473).—I. *Activation of Living Yeast by Yeast Extract or Preparations of Yeast Extract.*—In connexion with the investigations of Euler and Berggren (A., 1913, i, 145) and Harden and Young (A., 1914, i, 237), the author adduces new evidence to show that alcoholic fermentation by fresh top-yeast is greatly accelerated by activators, presumably co-enzymes, which are present in aqueous yeast extract, and that the phenomenon is observed when the number of cells in the fermenting liquor undergoes no, or very slight, increase. The activation of dry yeast by the co-enzyme is almost independent of the acidity of the solution in the region $P_H=3$—7.

II. *Activation of Living Yeast by Salts of Organic Acids.*—In contrast to Harden and Young, the author finds that the increase in the number of cells due to the addition of alkali formate never exceeds the experimental error involved in counting. On the other hand, it is shown that alcoholic fermentation by fresh top-yeast is greatly accelerated by ammonium or alkali formate. H. W.

Regeneration of Saccharase in Pre-treated Yeast. HANS VON EULER and OLOF SVANBERG (*Zeitsch. techn. Biol.*, 1919, 7, 165—172; from *Chem. Zentr.*, 1920, i, 473).—The authors have investigated the length of period necessary for the re-formation of enzyme-content removed by previous treatment; the results so far obtained do not permit a definite conclusion to be drawn. H. W.

Ferment Action. VI. A. FODOR (*Fermentforsch.*, 1920, 3, 193—200; from *Chem. Zentr.*, 1920, i, 471—472. Compare Abderhalden and Fodor, A., 1919, i, 369).—An active colloidal mixture can be separated from yeast extract by the addition of twice its volume of absolute alcohol; the precipitate (*R*) is separated after twelve hours and thoroughly washed with alcohol. It is not completely dissolved by protracted treatment with water at 37°, but leaves a residue (*r*), which yields a clear, golden-yellow solution with dilute sodium hydroxide, from which it does not separate on treatment with excess of acid. Whilst *R* contains the colloids of yeast extract, the aqueous-alcoholic filtrate is free from them, and is completely inactive fermentatively. The aqueous extract from *R* is readily coagulated when heated and, when cautiously acidified, deposits a perfectly white precipitate. It causes the fission of glycyl-*l*-leucine, but its activity is small in comparison with that of the original yeast extract. The solution also contains magnesium and phosphoric acid ions and, when rendered alkaline with sodium hydroxide, gives a crystalline precipitate of magnesium sodium phosphate and some magnesium ammonium phosphate in the same manner as the original extract. The residue, *r*, consists mainly of denatured proteins which are precipitated when the solution in alkali is acidified (owing to the action of the salt). According to the nitrogen content, this product differs from that precipitated by acids from the aqueous extract of *R*, though each is to be regarded as a nucleoprotein.

If alcohol is added to the yeast extract after removal of phosphate by addition of alkali, a precipitate, R_1, is obtained, which leaves a residue, *r*, after treatment with water. The faintly alkaline aqueous filtrate is not noticeably coagulated by heat even after neutralisation, yields at most an opalescence when cautiously acidified with hydrochloric acid, and is completely inactive towards glycyl-*l*-leucine even after addition of magnesium phosphate solution, the favourable influence of which on fermentative activity has been frequently demonstrated. The product, r_1, closely resembles *r*, and has the same nitrogen content. In the dry condition neither can function as acid or base in the sense of the ionic theory, though each acquires this property after hydration and increase of surface, which slowly occurs under the influence of acid or alkali. If more concentrated alkali hydroxide is used in reprecipitation, elimination of phosphoric acid occurs, even to such an extent that the substance becomes free from phosphorus; the nitrogen content is simultaneously altered.

In connexion with the present and previous investigations, the development of ferment action is explained on a colloidal chemical

basis. The union of the ferment, a negatively charged colloid, by adsorption with the substrate, activates the elements necessary for the hydrolysis of the latter by bringing them into the ionic condition. This happens as a consequence of the partial diminution of the adsorption potential of the colloidal particles by the opposite charge of the substrate. The optimal hydrogen-ion concentration depends on the individual properties of the ferment colloids and the amphoteric substrate and their mutual relationships. In the case of ferments which are active in alkaline solution, this becomes more displaced towards the alkaline side as the difference in acidic nature between the colloid and the substrate increases. H. W.

The Products of the "Acetone-*n*-Butyl Alcohol" Fermentation of Carbohydrate Material, with Special Reference to some of the Intermediate Substances Produced. JOSEPH REILLY, WILFRED JOHN HICKINBOTTOM, FRANCIS ROBERT HENLEY, and AAGE CHRISTIAN THAYSEN (*Biochem. J.*, 1920, **14**, 229—251).—In a normal fermentation of maize mash the acidity rises until a maximum is reached from thirteen to seventeen hours after inoculation. After this point is reached there is a very marked acceleration in the rate of production of acetone, *n*-butyl alcohol, carbon dioxide, and hydrogen, the acidity falling gradually to a constant value. The greater part of the acids produced are volatile in steam, and butyric and acetic acids were identified in the distillate. These acids are probably intermediate products in the production of acetone and butyl alcohol. Evidence in support of this is given by the results of carrying on the fermentation in the presence of calcium carbonate, when practically no acetone or butyl alcohol was obtained.

When acetic acid or ethyl acetoacetate is added to the fermenting mash an increased yield of acetone is obtained. Addition of formic acid and trichloroacetic acid appeared to inhibit fermentation, whilst propionic and butyric acids are converted into the corresponding alcohols.

A tentative suggestion of the action is put forward, in which acetic acid is considered as a monoketide, $H\cdot CH_2\cdot CO\cdot OH$. By condensation $CH_2{:}CO$ yields $CH_2{:}C(OH)\cdot CH{:}CO$, which by elimination of CO_2 and the addition of the elements of water would yield acetone. Similarly, the increased yield of acetone from acetoacetic acid may be explained on the assumption that this substance possesses the structure of a diketide. This hypothesis may be extended and is capable of explaining ordinary alcoholic fermentation. No direct evidence was obtained of the formation of acetaldehyde or of formic acid as an intermediate product in the acetone fermentation.
J. C. D.

Influence of a Reduced Amount of Potassium on the Physiological Characters of Sterigmatocystis nigra [Aspergillus niger]. M. MOLLIARD (*Compt. rend.*, 1920, **170**, 949—951).—When all but one-eightieth of the potassium phosphate

in the normal culture medium is replaced by sodium phosphate, the growth of *Aspergillus niger* is very slow and the yield of mycelium is very small. The sugar is to a large extent oxidised, but instead of giving almost entirely carbon dioxide, an important amount of oxalic acid is formed, the amount increasing regularly so long as there is any sugar left in the culture medium. Other points noted are the more rapid disappearance of the dextrose than of the lævulose, the total absence of conidiæ and of the black pigment, formation of a golden-yellow pigment diffusing into the medium, and the production of a substance soluble in the culture solution and giving a blue colour with iodine. W. G.

The Utilisation of α-Methylglucoside by Aspergillus niger. ARTHUR W. DOX and G. W. ROARK, jun. (*J. Biol. Chem.*, 1920, **41**, 475—481).—*Aspergillus niger* grows very poorly on media containing α-methylglucoside as the only source of carbon, but readily on sucrose media in the presence of the glucoside. More rapid utilisation of the glucoside occurs on the sucrose-free medium when the culture inoculated is a vigorous one, or one which has previously been growing in the presence of both sucrose and the glucoside. A gradual cumulative adaptation could not be demonstrated with certainty. J. C. D.

Synthesis of Aromatic Amino-acids in the Living Cell. L. HUGOUNENQ and GABRIEL FLORENCE (*Bull. Soc. chim. biol.*, 1920, **2**, 13—18).—*Aspergillus niger* produces proteins containing the aromatic amino-acids when growing on culture media containing inorganic nitrogen, sucrose, and tartaric acid. It is possible that it is able to utilise the carbon chain of a pentose for these synthetic processes. Probably the products of assimilation are broken down into substances of small molecular dimensions before the synthetic processes are commenced, and a parallel is drawn with the metabolic and anabolic processes in the higher animals. J. C. D.

Photo-synthesis in Fresh-water Algæ. I. The Fixation of Both Carbon and Nitrogen from the Atmosphere to Form Organic Tissue by the Green Plant Cell. II. Nutrition and Growth Produced by High Gaseous Dilutions of Simple Organic Compounds, such as Formaldehyde and Methyl Alcohol. III. Nutrition and Growth by means of High Dilutions of Carbon Dioxide and Oxides of Nitrogen without Access to Atmosphere. BENJAMIN MOORE and T. ARTHUR WEBSTER (*Proc. Roy. Soc.*, 1920, [*B*], **91**, 201—215).—Experimental evidence is given in support of the view that the lowest type of synthesising cell existing, namely, the unicellular alga, possesses the power of fixing carbon and nitrogen and building these up into reduced organic compounds with uptake of energy, the source of the energy being the sunlight. It is shown that formaldehyde or methyl alcohol fed to such a

! at a sufficiently high dilution can be used as a nutrient source carbon in absence of carbon dioxide, and very marked growths ve been obtained with these substances as the sole source of bon. In the absence of all other sources of nitrogen except atmospheric nitrogen, but with abundance of carbon dioxide, unicellular algæ can fix nitrogen, grow, and form proteins. e rate of fixation and growth is, however, greatly accelerated if rites or oxides of nitrogen are available, and the latter may be plied in the gaseous form from the atmosphere. W. G.

The Inhibition of Invertase in the Sap of Galanthus ralis. T. G. MASON (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, –97).—Experiments with the sap of the leaves of *Galanthus alis*, extracted under varying conditions, indicate that factors ibiting the activity of the invertase may be present in the sap. anges of a nature not yet clearly understood occur in the sap er its extraction from the leaf, which lead to a clumping of the oids, and possibly the enzyme may be inactivated by adsorption the coagulated colloids. W. G.

Presence of Gentianose and Sucrose in various Gentians. RC BRIDEL (*J. Pharm. Chim.*, 1920, [vii], **21**, 306—311; *Bull. . chim. biol.*, 1920, **2**, 37—41). Compare A., 1913, i, 149, 434,).—The author has detected the presence of both gentianose and rose in the roots of *Gentiana cruciata* and *G. purpurea*. The ersible change between gentianose and sucrose is governed by activity of the enzyme gentiobiase. W. P. S.

Anthocyanins. I. The Anthocyanins of the Young aves of the Grape Vine. OTTO ROSENHEIM (*Biochem.* 1920, **14**, 178—188).—The red pigment of the young leaves of grape vine is probably identical with oenidin, the anthocyanidin ived from the pigment of the purple grape. This is the first case ch has been noted in which the red pigment of the leaves is a anthocyanidin, and the European species *Vitis vinifera* appears e the only representative of the family *Vitis* which is so charac- sed. The occurrence of a colourless modification of the pigment demonstrated, for which the general name *leucoanthocyanin* is posed. It is present in combination possibly with carbohydrate, is converted into anthocyanidin by strong acids. J. C. D.

Distribution of Lycorine in the N.O. Amaryllidaceæ. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], **1**, 352—358). he first accurate description of an alkaloid of this order refers lycorine from *Lycoris radiata*, Herb. (Morishima, A., 1899, 2), and this is identical with narcissine (Ewins, T., 1910, **97**. 6) from *Narcissus pseudonarcissus*, L. (compare Asahina and ii, A., 1913, i, 1093). The latter name should therefore be ndoned; the formula of the alkaloid is $C_{16}H_{17}O_4N$ (Ewins), with ch the analytical results of Morishima agree better than with

the formula $C_{32}H_{32}O_9N_2$ proposed by him, which is, moreover, excluded by molecular-weight determinations (Ewins, Asahina, and Sugii). The alkaloid of *Buphane disticha*, Herb. (Tutin, T., 1911, **99**, 1240) is also lycorine, as is that in *Narcissus Tazetta*, L. (Yamanouchi, *Arch. Pharm.*, 1913, **251**, 357). Gorter has further found lycorine in *Zephyranthes rosea*, Lindl, *Crinum asiaticum*, L., *C. giganteum*, Andr., *C. pratense*, Herb., *Hymenocallis littoralis*, Salisb., *Eucharis grandiflora*, Planch., and *Eurycles sylvestris*, Salisb. *Crinum* spp. contain most (0·1—0·18% of bulb). G. B.

A New Plant containing Coumarin: Melittis melissophyllum, L. P. Guérin and A. Goris (*Compt. rend.*, 1920, **170**, 1067—1068).—The leaves of *Melittis melissophyllum*, L. contain coumarin apparently in the form of a glucoside decomposable by emulsin. The coumarin may be extracted along with quercetin from the dried leaves by 95% alcohol. W. G.

Constituents of Morinda citrifolia. John Lionel Simonsen (T., 1920, **117**, 561—564).

***Acidity and Acidimetry of Soils. I. Studies of the* Hopkins and Pettit Method for Estimating Soil Acidity** Henry G. Knight (*J. Ind. Eng. Chem.*, 1920, **12**, 340—344).—Investigation of this method (extraction with potassium nitrate solution and titration of the extract) showed that an acid soil gives the same acidity whether it is extracted with *N*/1-potassium nitrate, *potassium chloride, sodium nitrate, sodium chloride, or calcium* chloride solution. The acidity of the salt extract of an acid soil is independent of the temperature within the range of 25° to 90°, but the acidity of the first portions of the extract increases with increase of the concentration of the salt solution. The difference *in absorption of calcium and potassium from solutions of their* bases by an acid soil may be due to precipitation. There is a basic exchange when a salt solution is added to an acid soil; alumina is dissolved, but this does not account for the total acidity of the solution. Exchange of acid radicles is slight or does not occur. W. P. S.

Hysteresis of Aqueous Suspensions of Humus Earth. Heinrich Puchner (*Kolloid Zeitsch.*, 1920, **26**, 159—168. Compare this vol., i, 274).—A continuation of the previously published work. *The present paper deals particularly with hysteresis pheno-*mena occurring in the insoluble portion obtained from the settling of suspensions of peat in water. It is shown that the delayed effects observed are due, not only to physical and chemical processes, but are very largely influenced by the growth of low forms of plant life. J. F. S.

Organic Chemistry.

Positive Halogen in Organic Compounds. Iodine in Di-iodoacetylene and Chloroiodoethylene. LLOYD B. HOWELL [with WILLIAM A. NOYES] (*J. Amer. Chem. Soc.*, 1920, **42**, 991—1010).—It is suggested that the reactivity of halogen substitution derivatives of acetylene is due to the quadrivalence of the carbon atom rather than to the presence of a bivalent carbon atom (Nef, A., 1898, i, 102), and also to the positive character of the halogen atom, also exemplified when halogen replaces hydrogen in *amino-*, *imino-*, or *hydroxyl groups*. In agreement with this, di-iodoacetylene is shown to be produced by the action of iodine monochloride on calcium carbide or copper acetylide, although acetylene itself gives *a*-chloro-*β*-iodoethylene (Plimpton, T., 1882, 392). Further, di-iodoacetylene is decomposed by neutral, more quickly by acid, solutions of potassium iodide, with formation of acetylene, iodine, and potassium hydroxide. Although nitrogen iodide is considered to contain positive iodine atoms (Chattaway, A., 1900, ii, 722), it could not be obtained from di-iodoacetylene by means of ammonia, but this is not surprising, since acetylene is iodinated by the iodide (Datta and Prosad, A., 1917, i, 332). The formation of hexachloroethane by the action of chlorine on di-iodoethylene (Biltz, A., 1897, i, 389) is preceded by the production of the very unstable compound, $C_2Cl_4I_2$, yellow needles, which apparently melt, but probably decompose, at 42—43°. It decomposes in the dark, even at temperatures below 0°, within a few minutes, giving *as*-dichlorodi-iodoethylene, iodine trichloride, and traces of a liquid, b. p. 80—84°/32 mm., probably trichloroiodoethylene. This result, the formation of di-iodoacetylene by the action of alcoholic potash, and the fact that the whole of the iodine is not converted into iodide by treatment with lime or sodium peroxide, indicate that the compound is *aβ-dichloro-β-iodoethylene a-iododichloride*, $CICl:CCl \cdot ICl_2$. s-*Dichlorodi-iodoethylene*,

$$CICl:CICl,$$

is an odourless, pale yellow liquid, b. p. 127·5—128·5°/25—26 mm., or 243·5° (corr. decomp.)/760 mm., which solidifies slightly below 0°. It reacts with difficulty with hot alcoholic silver nitrate solution, and gives di-iodoacetylene when treated with alcoholic potash. With chlorine, it gives an *iododichloride*, $CICl:CCl \cdot ICl_2$, a yellow compound, which liberates one molecular proportion of iodine from potassium iodide. The course of the chlorination of di-iodoacetylene is therefore represented as follows: $C_2I_2 \longrightarrow [CI:C \cdot ICl_2] \longrightarrow CICl:CICl \longrightarrow CICl:CCl \cdot ICl_2 \longrightarrow [CICl_2 \cdot CICl_2] \longrightarrow C_2Cl_6 + 2ICl \longrightarrow 2ICl_3$. *a*-Chloroethylene *β*-iododichloride is produced by passing acetylene through a solution of iodine trichloride in hydrochloric acid; freshly crystallised from methyl alcohol, it melted at

66° (decomp.), but after several hours at 80°. Contrary to the statement of Thiele and Haakh (A., 1909, i, 865), its decomposition does not result in the formation of chlorine, but of iodine, iodine monochloride, and a number of liquid halogen compounds, of which the chief is *αββ*-trichloro-*α*-iodoethane; no trace of *as*-chloroiodoethylene could be discovered. Iodine trichloride as usually prepared contains a large quantity of the monochloride. A very satisfactory method of preparing solutions of the trichloride in hydrochloric acid consists in the addition of a finely ground mixture of iodic acid (3 mols.) and re-sublimed iodine (1 mol.) to a cooled solution of twice the theoretical volume of hydrochloric acid (D 1·19). Such solutions may be kept indefinitely, even at 30°. The positive character of the iodine atom in nitrogen tri-iodide is illustrated by the formation of iodine monochloride on addition of concentrated hydrochloric acid to the tri-iodide. J. K.

Vapour Composition of Mixtures of Ethyl Alcohol and Water. W. K. LEWIS (*J. Ind. Eng. Chem.*, 1920, **12**, 496—499).—The vapour composition of mixtures of ethyl alcohol and water was determined by Vrevski (A., 1912, ii, 1139) under varying pressures at 40°, 55°, and 75°. These results have been recalculated and extended by extrapolation up to the boiling points of the liquids. The vapour composition curve is shown diagrammatically, whilst the change in the vapour composition with the alteration in the boiling point has been determined from the slope of the temperature curves and plotted in a diagram, so as to be applicable to pressures other than the atmospheric pressure. The total pressure exerted by a given mixture of ethyl alcohol and water at a given temperature, divided by the pressure of pure water at the same temperature, forms a ratio which changes but little with a change in the temperature. The value of this ratio rises rapidly from water (as unity) with each increase of alcohol to about 2·3 for pure ethyl alcohol. The value of this ratio at the boiling point is plotted as a separate curve to enable the relationship between pressure and temperature to be made under other conditions than atmospheric pressure, as, for example, in the lower part of a rectifying column. C. A. M.

The Ceryl Alcohol and Cerotic Acid of Chinese Wax. ALBERT GASCARD (*Compt. rend.*, 1920, **170**, 1326—1328).—Ceryl cerotate, as isolated from Chinese wax and carefully purified, has m. p. 84°. When hydrolysed, the ceryl alcohol obtained therefrom has m. p. 80°, and gives an iodide, m. p. 59°. Analysis of the iodide and the behaviour of the iodide when treated with sodium amalgam confirm Brodie's formula, $C_{27}H_{55}\cdot OH$, for this alcohol. Similarly, the cerotic acid, m. p. 82—82·5°, isolated from the products of hydrolysis, is shown to have the formula $C_{26}H_{53}\cdot CO_2H$. W. G.

Catalytic Preparation by the Dry Way of certain Ethers. ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1920, [iv], **27**, 328—330. Compare this vol., i, 6, 284).—When allyl alcohol

vapour is passed over calcined alum at 185—190°, a 30% yield of allyl ether is obtained. When the allyl alcohol is mixed with methyl alcohol or its four higher homologues, a certain amount of the mixed ethers is obtained, but the main product is allyl ether; in no case, however, is any appreciable amount of methyl ether or its homologues obtained. Under similar conditions, benzyl alcohol did not give benzyl ether, but a yellow, resinous compound, $(C_7H_6)_n$, but when the benzyl alcohol was mixed with methyl or ethyl alcohol, some mixed ether resulted. W. G.

Decomposition of Nitric Esters. ROBERT CROSBIE FARMER (T., 1920, **117**, 806—818).

The History of Zeise's Mercaptan and its Name. O. ZEISE (*J. pr. Chem.*, 1919, [ii], **100**, 48).—A personal note arising from Diergart's recent communication (this vol., i, 137) under the above title. H. W.

Crystallographic Properties of Sulphonal. H. SEIFERT (*Centr. Min.*, 1920, 97—101).—Sulphonal (diethylsulphondimethylmethane), $CMe_2(SO_2Et)_2$, crystallises in the *monoclinic* system, and is pseudo-rhombic in character; $a:b:c = 1.563:1:1.416$, $\beta = 90°31\frac{1}{2}'$. Crystals were examined grown from water, aqueous alcohol, ether, ethyl acetate, chloroform, carbon tetrachloride, and toluene; the habit of the crystals varies considerably according to the solvent from which they are grown. The crystals are generally well developed polyhedra, but from toluene or alcohol skeleton crystals are frequently obtained. Striations and vicinal faces sometimes appear. There is a good cleavage parallel to $a\{100\}$, and the crystals show considerable plasticity. They are colourless and show negative double refraction, the optic axial plane being $b\{010\}$. E. H. R.

***n*-Butyl Chloroformate and its Derivatives.** FREDERICK DANIEL CHATTAWAY and EDOUARD SAERENS (T., 1920, **117**, 708—711).

The Use of αβ-Dichlorovinyl Ethyl Ether for the Production of Chloroacetates and Acid Chlorides. HOLLAND CROMPTON and PAULE LAURE VANDERSTICHELE (T., 1920, **117**, 691—693).

Leucic [α-Hydroxy*iso*hexoic] Acid and Walden's Inversion of Leucic Acid. SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1919, **40**, 825—862).—Certain amino-acids, for example, glutamic acid and its salts, are extensively used in Japan as taste-promoting substances in food. The author has obtained very sweet substances by de-aminising leucine. Crude leucine hydrochloride, prepared by the hydrolysis of protein, is dissolved in several volumes of water and de-aminised; calcium oxide precipitates crude calcium α-hydroxy*iso*hexoate, which is suspended in water and treated with

sodium hydrogen carbonate, the filtrate giving *sodium α-hydroxy-isohexoate*, long plates (from alcohol), after concentration. This salt, as well as the ammonium, potassium, sodium hydrogen, potassium hydrogen, and calcium salts, is exceedingly sweet, being about ten times sweeter than sucrose. Since all the salts and the acid in dilute solution are sweet, whilst the solid acid and its ester are not, the taste must be due to the α-hydroxy*iso*hexoic ion. Neither Cohen's dulcigenn nor Oertly and Meyer's glucophore is present in the α-hydroxy*iso*hexoic acid molecule. Its use is recommended as a substitute for calcium lactate or "saccharin."

The influence of substituents on the sweetness has also been investigated. Both the anhydrides, $C_4H_9{\cdot}CH{<}{}^{CO{\cdot}O}_{O{\cdot}CO}{>}CH{\cdot}C_4H_9$ and $C_4H_9{\cdot}CH(OH){\cdot}CO{\cdot}O{\cdot}CH(CO_2H){\cdot}C_4H_9$, are bitter, but become sweet by boiling with alkalis. The acetyl derivative tastes like ether; its calcium salt is tasteless, but becomes sweet at 100°, owing to the formation of calcium α-hydroxy*iso*hexoate. Alkyl-leucic acids and their salts resemble the acetyl derivative.

The author has found that *d*-glutamic acid is twice as sweet as the *dl*-acid, and also that the sweetness of a metallic α-hydroxy*iso*hexoate becomes more pronounced the less the lævorotation of the salt. In accordance with this, *d*-α-hydroxy*iso*hexoic acid, prepared from the *l*-acid by Walden's inversion, gives *d*-salts, which are sweetest of all; the *dl*-acid, which is also produced during the inversion, is sweeter than the *l*-acid.

The following substances are described. l-α-*Chloro*iso*hexoyl chloride*, b. p. 59°/11 mm., is slightly lævorotatory; in benzene solution its rotation approaches zero, and then becomes dextrorotatory by further dilution. l-α-*Chloro*iso*hexoic acid* has b. p. 113·5—114°/10 mm., and [α] −19·8° in 5% alcoholic solution; the ethyl ester has b. p. 79—80°/10 mm. and [α] −18·4°, and the anilide, needles, decomposes at 95—96°. *Sodium* l-α-*hydroxy*iso-*hexoate* has [α] −25·3°, the *potassium* salt, m. p. 72°, has [α] −21·6°, and the *sodium hydrogen* salt,

$$C_6H_{11}O_3Na,C_6H_{12}O_3,2H_2O,$$

has $[\alpha]^{20}$ −28·0° (tungsten light). CHEMICAL ABSTRACTS.

Action of Heat on Oxalic Acid and Oxalates. G. CALCAGNI (*Gazzetta*, 1920, **50**, i, 245—251).—Hydrated oxalic acid melts at 98° and yields a mixture of carbon monoxide and dioxide, but not in equal volumes, at 110—120°. The anhydrous acid cannot be obtained by keeping the hydrated acid at a temperature somewhat above 100°, as the acid then sublimes and decomposes. Storage of the hydrated acid for several months in a vacuum desiccator over sulphuric acid yields an anhydrous compound, which begins to become pasty and to decompose at 135°, complete fusion and vigorous decomposition and distillation occurring at 160°. The melting point, given as 186—187° by Staub and Smith and as 189·5° by Althaussen and Bamberger, could not be confirmed. The products yielded when various oxalates are decomposed by heat have also been investigated. [See *J. Soc. Chem. Ind.*, 1920, 501A.]

T. H. P.

Preparation of Formaldehyde. MOYER DELWYN THOMAS (*J. Amer. Chem. Soc.*, 1920, **42**, 867—882).—The oxidation of methyl alcohol to formaldehyde by passing a mixture of air and methyl alcohol vapour over spirals of copper, silver, and gold, respectively, at 400° has been investigated. It is shown that silver is a more active catalyst than copper or gold in the dehydrogenation of methyl alcohol, and at the same time it produces less decomposition of the formaldehyde, so that the yield of formaldehyde is very much greater with silver than with gold or copper. With silver, an absolute yield of 95% and a process yield of 55·6% were obtained when the reaction mixture contained 0·25 gram of oxygen per gram of alcohol. Under similar conditions with gold, the absolute yield was 90·5% and the process yield 50·5%, whilst the values for copper were 88·5% and 40% respectively. The best process yields were obtained with silver and gold, when the reaction mixture contained 0·4—0·5 gram of oxygen per gram of alcohol. With copper, this value was higher, 0·55—0·65 gram of oxygen per gram of alcohol. The optimum speed of the air for all three catalysts was 125—150 litres per hour. The length of the catalyst spiral did not exert a very marked influence on the process. The temperature of the reaction was measured for gold, and found to vary between 520° and 900°, according to the conditions, although the spiral was only heated to 400° to start the reaction, and then the heating was stopped. Using gold, 1·7% of acetone or 10% of water in the alcohol did not appreciably influence the process. The process consists in dehydrogenation, followed by the oxidation of hydrogen and carbon monoxide. J. F. S.

Physico-chemical Studies of Mixtures of Water, Acetaldehyde, and Paracetaldehyde. PAUL PASCAL and DUPUY (*Bull. Soc. chim.*, 1920, [iv], **27**, 353—362).—The authors have determined the solubility of paracetaldehyde in water, and of water in paracetaldehyde over the temperature range 6—85°, and have shown that the solubility of paracetaldehyde in water is much diminished by the presence of 5% of sulphuric acid. The relative solubility of acetaldehyde in paracetaldehyde and in water increases with rise in temperature, and still further increases if sulphuric acid is present in the water.

Finally, the authors have determined the densities (D_4^t and D_4^{20}) of paracetaldehyde and mixtures of paracetaldehyde and water, acetaldehyde and water, and acetaldehyde and paracetaldehyde in varying proportions. W. G.

Action of Hydrocyanic Acid on Dextrose; Kiliani's Reaction. J. BOUGAULT and J. PERRIER (*Compt. rend.*, 1920, **170**, 1186—1189).—The combination of hydrogen cyanide with dextrose to give ammonium glucoheptonate does not take place in a feebly acid medium. A trace of alkali is sufficient to start the action, which is then continuous,

$$C_6H_{12}O_6 + KCN + 2H_2O = C_6H_{13}O_6 \cdot CO_2K + NH_3.$$

It is shown that the action of potassium cyanide on dextrose i bimolecular. W. G.

Purification of Celluloses. Action of Alkaline Earth on their Incrustations and on Hydro- and Oxy-celluloses CARL G. SCHWALBE and ERNST BECKER (*J. pr. Chem.*, 1919, [ii **100**, 19—47).—The action of the hydroxides of calcium, strontiur and barium, and of magnesium oxide on a number of hydro- an oxy-celluloses has been investigated, the actions generally bein carried out at the boiling point of the solutions at the ordinar pressure. The authors are led to the following conclusion: Hydro- and oxy-celluloses are mixtures of celluloses and the degradation products. In the case of the hydrocelluloses fro cotton or from wood, the latter are present in amounts of abo 24—36%. Bleaching powder oxycellulose contains about 60% pure cellulose and 40% of apparently oxidised degradation pr ducts. Sulphite celluloses contain cellulose dextrins, eith naturally or formed during the process of boiling, which can l removed by boiling with lime. A variety of cellulose which practically without reducing power is obtained by the action boiling milk of lime on all sulphite celluloses, hydro- and ox celluloses. Sulphite wood celluloses lose up to 50% of the pentosan content when boiled with lime, whilst also the meth content is depressed, sometimes to a considerable extent; the re due, however, still retains pentosans in very stable combinatio Treatment with lime removes but little from soda wood cellulos since any cellulose dextrins which may be present are dissolv during the boiling with alkali. [See, further, *J. Soc. Chem. In* 1920, July.] H. W.

Lignin and Reactions of Lignin. PETER KLASON (*Ber.*, 19 **53**, [*B*], 706—711. Compare this vol., i, 148).—Further exami ation of β-naphthylamine lignosulphonate leads the author to ascri to it a constitution different to that previously given, since it is n shown that only a portion of the β-naphthylamine is precipita when the salt is gently warmed with dilute alkali, and that salt is readily regenerated by the addition of β-naphthylamine hyd chloride to the filtered solution. The formation of the salt is c sidered to indicate the presence of the group R·CH:CH·CHO lignin, and reaction is formulated according to the scheme

$$R\cdot CH{:}CH\cdot CHO + H\cdot SO_2\cdot OH = R\cdot CH_2\cdot CH(SO_2\cdot OH)\cdot CHO \xrightarrow{+C_{10}H_7\cdot}$$

$$R\cdot CH_2\cdot CH(SO_2\cdot O\cdot NH_3\cdot C_{10}H_7)\cdot CHO \longrightarrow$$

$$R\cdot CH_2\cdot CH{<}^{SO_2\text{-}O}_{CH:NH\cdot C_{10}H_7} + H_2$$

The compound is thus an internal ammonium salt in which opening of the ring under the influence of alkali can occur either of two directions, yielding either the alkali salt of the a $R\cdot CH_2\cdot CH(\cdot CH{:}N\cdot C_{10}H_7)\cdot SO_3H$, or the alkali salt of lig sulphonic acid and free β-naphthylamine. The salt is formed

greater quantity from old than from fresh sulphite liquors, so that it would appear that the group R·CH:CH·CH_2·OH is present in the latter, and that the aldehyde is gradually formed in them by atmospheric oxidation.

The simplest aromatic substances containing these groups are cinnamaldehyde and cinnamyl alcohol. The colorations given by the former with phloroglucinol and Wiesner's reagent closely resemble those obtained with lignin. Also, when it is treated with the sulphite acid solution at 100° and the "reversible" sulphite is removed, the residual solution readily yields the cyclic salt,

$$CH_2Ph\cdot CH{<}{\scriptstyle SO_2\cdot O \atop \scriptstyle CH:NH\cdot C_{10}H_7}{\rceil}$$

on treatment with β-naphthylamine hydrochloride, the properties of which are strikingly similar to those of β-naphthylamine ligninsulphonate.

A consideration of these results and of others obtained by himself and different investigators leads the author to the conclusion that a hypothetical coniferylaldehyde (and coniferyl alcohol) are the most important and sole chemically active constituents, at any rate of coniferous lignin. H. W.

Some Synthetic Peptides. (MLLE) L. PETRESCU (*Bul. Soc. Chim. România*, 1919, **1**, 56—60).—Phenylaminoacetic acid, when condensed with bromoacetyl chloride, yields *bromoacetylphenylglycine*, CH_2Br·CO·NH·CHPh·CO_2H, m. p. 140°, which, when treated with ammonia, gives *glycylphenylglycine*,

NH_2·CH_2·CO·NH·CHPh·CO_2H,

m. p. 226°, giving a *copper* salt and an anhydride, 3:6-*diketo-2-phenylpiperazine*, $CH_2{<}{\scriptstyle CO\cdot NH \atop \scriptstyle NH\cdot CO}{>}CHPh$, m. p. 232°. W. G.

New Preparation of Amines by Catalysis. A. MAILHE (*Compt. rend.*, 1920, **170**, 1120—1123).—When the aldazines, obtained by the condensation of aldehydes with hydrazine, are passed together with hydrogen over reduced nickel at 140—160°, they do not yield symmetrical hydrazines, but the corresponding primary and secondary amines, the relative proportions of the two amines obtained varying with the temperature of hydrogenation and the aldazine used. W. G.

Catalytic Hydrogenation of Ketazines. A. MAILHE (*Compt. rend.*, 1920, **170**, 1265—1267. Compare preceding abstract).—By hydrogenation with reduced nickel as a catalyst, the ketazines yield primary amines at low temperatures and a mixture of primary and secondary amines at higher temperatures. Thus dimethylketazine at 130—131° yields *iso*propylamine, and, in larger amount, di*iso*propylamine. Diethylketazine, b. p. 160—163°, yields at 160—170° chiefly γ-*aminopentane*, CH_2Me·CH(NH_2)·CH_2Me, b. p. 84°, giving a *hydrochloride* and a *phenylcarbamide*, m. p. 148°. Di*iso*propylketazine at 170—180° gives, as the chief product, γ-*amino-ββ*-

dimethylpentane, $CHMe_2\cdot CH(NH_2)\cdot CHMe_2$, b. p. 125—127°, giving a *phenylcarbamide*, m. p. 139—140°. Dipropylketazine at 170° gives *δ-aminoheptane*, $CH_2Me\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot CH_2Me$, b. p. 135—136°, giving a *hydrochloride* and a *phenylcarbamide*, m. p. 134°. Diisobutylketazine at 215—220° yields *δ-amino-βζ-dimethylheptane*, $CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot CHMe_2$, b. p. 175—177°, together with some *di-diisobutylcarbinylamine*,

$$[(CHMe_2\cdot CH_2)_2\cdot CH]_2NH.$$

W. G.

The Acylation of Thiocarbamides. AUGUSTUS EDWARD DIXON and JOHN TAYLOR (T., 1920, **117**, 720—728).

New Methods of Synthesis of Nitriles by Catalysis. ALPHONSE MAILHE (*Ann. Chim.*, 1920, [ix], **13**, 183—228).—A résumé of work already published (compare A., 1917, i, 686; 1918, i, 68, 105, 256, 336, 389, 532; this vol., i, 224, 377, 378, 380).

W. G.

Electrolytic Preparation of Potassium Ferricyanide. O. W. BROWN, C. O. HENKE, and I. L. MILLER (*J. Physical Chem.*, 1920, **24**, 230—237).—The electrolytic oxidation of potassium ferrocyanide has been investigated. Using an undivided cell with electrodes of various shapes and with stirred and non-stirred solutions, the maximum yield was about 50%. When a diaphragm was used with a current density of 0·90 amp. per sq. dcm., potassium hydroxide was found in both compartments of the cell, and a current efficiency of about 98% was obtained. The presence of potassium hydroxide increases the current efficiency and decreases the voltage slightly. By leaving a space in the electrolysis vessel and operating a stirrer above the gauze anode, the ferricyanide can be forced below the electrode, where it crystallises, instead of on the anode, where it would cause voltage losses. All the ferrocyanide decomposed is not converted into ferricyanide. Different current efficiencies are obtained with different electrode materials, and in all cases the maximum current efficiency is reached when the electrolysis has been in progress for about four hours. The following maximum current efficiencies were obtained, working with an anode 7½ cm. × 11½ cm. and a current of 0·95 amp.: copper 96·3%, nickel 97·7%, platinum 96·6%, Acheson graphite 99·7%, and lead covered with lead dioxide 93%. J. F. S.

Action of Hydrazine Hydrate on Glycerides of Higher Fatty Acids. I. P. FALCIOLA (*Gazzetta*, 1920, **50**, i, 162—165. Compare Falciola and Mannino, A., 1915, i, 59).—The action of hydrazine hydrate on triolein, tristearin, and various other derivatives of oleic and stearic acids yields compounds which correspond perfectly in their chemical and physical properties with the hydrazides studied by Curtius (A., 1896, i, 34,* and elsewhere), and rapidly reduce Fehling's solution and ammoniacal silver nitrate solution. Further, the double linking of the oleic acid residue

appears to undergo hydrogenation during the action of the hydrazine hydrate, the compounds obtained from triolein and tristearin exhibiting the same melting point, which remains unaltered when the two compounds are mixed in various proportions. The identity of the two compounds is not definitely established, but they exhibit similar cryoscopic behaviour in *p*-nitrobenzaldehyde and similar ebullioscopic behaviour in benzene; further, the hydrazide obtained from triolein does not respond to the ordinary reactions for compounds with a double linking in the molecule.

The *hydrazide*, $C_{17}H_{35}\cdot CO\cdot NH\cdot NH_2$, obtained from tristearin, forms white leaflets, m. p. 115°, and that from triolein, white leaflets, m. p. 114·5—115°. Similarly, ethyl oleate yields a compound, m. p. 114—115°, and ethyl chloro-oleate or chlorostearate a compound, m. p. 111—114°.

With zinc and acetic acid, the two hydrazides yield a crystalline product of lower melting point, with permanganate in acetic acid a white *compound*, m. p. (crude) 70—76°, and with sulphuric and nitric acids together a *compound*, m. p. (crude) 55—60°.

T. H. P.

The Production of Ethylarsinic Acid. AMAND VALEUR and RAYMOND DELABY (*Bull. Soc. chim.*, 1920, [iv], **27**, 366—370).—The authors have repeated Dehn's work on the action of ethyl iodide on tripotassium arsenite in alcoholic solution (compare A., 1906, i, 341), and find that the action is much slower and less complete than is stated by that author. The ethyl iodide disappears much more rapidly than corresponds with the amount of arsenite converted into ethylarsinate. If the action is carried out in aqueous solution, there is not this loss of ethyl iodide, and the action is fairly complete at the end of twenty-five days. W. G.

New Mercury Compounds obtained by the Oxidation of Hydrazines by Mercuric Oxide. OTTO DIELS and SIBYLLE UTHEMANN (*Ber.*, 1920, **53**, [*B*], 723—731).—When an aqueous solution of ethyl hydrazinecarboxylate is treated with yellow mercuric oxide without precautions being taken to moderate the temperature, an energetic action occurs, and large volumes of gas are evolved, consisting mainly of nitrogen, but containing also carbon monoxide and small quantities of an odoriferous substance, which is probably ethyl azidoformate; the aqueous solution contains ethyl hydrazodicarboxylate, m. p. 130°, and a beautifully crystalline mercury salt, $C_{12}H_{20}O_8N_2Hg_2$, needles, m. p. 155°. The formula $CO_2Et\cdot N(Hg\cdot CO_2Et)\cdot N(Hg\cdot CO_2Et)\cdot CO_2Et$ is assigned to the latter, since it is decomposed by hydrochloric acid into mercuric chloride, ethyl hydrazodicarboxylate, carbon monoxide, and alcohol; by bromine in benzene solution into mercuric bromide, ethyl azodicarboxylate, and ethyl bromoformate, and by piperidine into mercury, ethyl hydrazodicarboxylate, and piperylurethane (ethyl piperidine-*N*-carboxylate). Methyl hydrazinecarboxylate reacts with yellow mercuric oxide in a precisely similar manner,

yielding methyl hydrazodicarboxylate and the mercury salt, $CO_2Me \cdot N(Hg \cdot CO_2Me) \cdot N(Hg \cdot CO_2Me) \cdot CO_2Me$, m. p. 215°.

The authors consider that their experiments lend some support to the hypothesis that di-imide or its derivatives are the primary products of the oxidation of hydrazines. In the present instance, they suppose that ethyl di-imidecarboxylate is first formed, $NH_2 \cdot NH \cdot CO_2Et + HgO = H_2O + Hg + NH{:}N \cdot CO_2Et$, which further reacts with mercuric oxide to yield the mercury salt,

$$Hg(N{:}N \cdot CO_2Et)_2.$$

The latter then exhibits the tendency common to many simply substituted hydrazines of passing into symmetrical disubstituted derivatives, and yields the product,

$$CO_2Et \cdot N{:}N \cdot Hg \cdot N(CO_2Et) \cdot N(CO_2Et) \cdot Hg \cdot N{:}N \cdot CO_2Et,$$

which in the manner of a diazonium compound loses nitrogen and gives the mercury salt. H. W.

Kinetics of the Chlorination of Benzene. F. Bourion (*Compt. rend.*, 1920, **170**, 1319—1321).—In the chlorination of industrial benzene in the presence of iron as a catalyst, the yield of monochlorobenzene increases with the velocity of chlorination. For a given time and a given concentration, the fraction of a molecule of benzene converted into monochlorobenzene is 8·5 times greater than the fraction of a molecule of chlorobenzene converted into *p*-dichlorobenzene. The yield of monochlorobenzene decreases slightly with rise in temperature. W. G.

The Chlorination of *m*-Dichlorobenzene. S. C. J. Olivier (*Rec. trav. chim.*, 1920, **39**, 411—413).—The principal product of the chlorination of *m*-dichlorobenzene in the presence of aluminium chloride is 1 : 2 : 4-trichlorobenzene. The results obtained confirm those of Cohen and Hartley (T., 1905, **87**, 1364), but refute those of Mouneyrat and Pouret (compare A., 1899, i, 263). W. G.

***o*-Chlorodinitrotoluenes. I.** Gilbert T. Morgan and Harry Dugald Keith Drew (T., 1920, **117**, 784—793).

Preparation of certain Iodo-compounds. Cuthbert William James, James Kenner, and Wilfrid Victor Stubbings (T., 1920, **117**, 773—776).

***p*-ββ-Dimethylpropylbenzenesulphonic Acid and certain of its Derivatives.** Artur Bygdén (*J. pr. Chem.*, 1919, [ii], **100**, 1—18).—α-Phenyl-ββ-dimethylpropane (A., 1913, i, 29) is converted by sulphuric acid containing 6% of sulphur trioxide into *p*-ββ-*dimethylpropylbenzenesulphonic acid*, $CMe_3 \cdot CH_2 \cdot C_6H_4 \cdot SO_3H$, the yield being about 95%; the acid forms long, colourless leaflets or large rectangular plates ($+2H_2O$), which, when preserved over concentrated sulphuric acid, are transformed into the *monohydrate*, m. p. 142·2—144·2° in an open, 145·6—146·6° (*corr.*) in a closed, capillary. The constitution of the acid is deduced from its conversion into *p*-hydroxybenzoic acid by oxidation with chromic acid

in dilute sulphuric acid, and subsequent fusion of the product with sodium hydroxide, and by its oxidation by permanganate to *p*-sulphobenzoic acid. The following salts are described: *potassium*, $+H_2O$; *rubidium*, $+H_2O$; *caesium*, $+\frac{1}{2}H_2O$; *sodium*, $+2H_2O$; *lithium*, $+H_2O$; *calcium*, $+\frac{1}{2}H_2O$; *strontium*, $+2H_2O$; *barium*, $+3H_2O$; *magnesium*, $+7H_2O$; *zinc*, $+6H_2O$; *cadmium*, $+3H_2O$; *ferrous*, $+7H_2O$; *nickel*, $+8H_2O$; *cobalt*, $+8H_2O$ (?); *lead*, $+2H_2O$; *copper*, $+6H_2O$; *silver*, $+1H_2O$; *ammonium*, anhydrous; *methylammonium*, $+\frac{1}{2}H_2O$, m. p. about 225° after much softening at about 150°; *ethylammonium*, m. p. 114—115° (corr.) after previous softening; *brucine*, m. p. 211·0—212·0° (corr.). p-ββ-*Dimethylpropylbenzenesulphonyl chloride* forms colourless, rectangular plates or prisms, m. p. 58·7—59·2° (corr.), whilst the corresponding *bromide*, plates, has m. p. 65·5—66° (corr.). The sulphonyl chloride is converted in the usual manner into the *amide*, needles, m. p. 101° (corr.), the *methylamide*, rhombic plates, m. p. 94·8—95·3° (corr.), the *anilide*, monoclinic plates, m. p. 137° (corr.), the *methylanilide*, colourless needles, m. p. 97·8—98·0° (corr.), the o-*toluidide*, thin, shining leaflets, m. p. 156—157° (corr.), the p-*toluidide*, rhombic plates, m. p. 117·9—118·2° (corr.), and the *benzylamide*, six-sided plates or colourless needles, m. p. 141·5—141·7° (corr.). p-ββ-*Dimethylpropylphenol*, $CMe_3{\cdot}CH_2{\cdot}C_6H_4{\cdot}OH$, small needles, m. p. 118·0—118·2° (corr.), is obtained by fusing potassium *p*-ββ-dimethylpropylbenzenesulphonate with potassium hydroxide, and subsequent acidification of the product. H. W.

Preparation of *p*-Phenylenediamine and Aniline from their corresponding Chlorobenzenes. ARMAND J. QUICK (*J. Amer. Chem. Soc.*, 1920, **42**, 1033—1042).—The catalytic influence of copper salts on the reaction between ammonia and chlorobenzene (D.R.-P. 204951) or *p*-dichlorobenzene (D.R.-P. 202171) is not connected with the formation of copper ammonium compounds, since nickel, cobalt, and zinc salts, which form similar compounds, have no influence. Cuprous are more effective than cupric salts, which probably only become effective when reduced, and water cannot be replaced by alcohol as a solvent in the reaction. The reaction with dichlorobenzene is best carried out above 200°; with 5—6% solutions of ammonia, the reaction is very incomplete, and an amorphous, red product is also produced. Addition of iron filings or activated charcoal to the cuprous salt improves the appearance of the final product, but with concentrated solutions of ammonia they, particularly the former, tend to retard the reaction. The action of ammonia on chlorobenzene under the conditions prescribed gave only a 39% yield, as against 80% claimed by the patent. Increase in concentration of ammonia beyond 14%, or in working temperature beyond 200°, does not improve the yield, although the latter is necessary for complete decomposition of the chlorobenzene. Cuprous iodide has no catalytic value for this reaction. Diphenylamine could not be

obtained from bromobenzene under the conditions prescribed by D.R.-P. 187870. J. K.

Nitration of Aceto-*m*-toluidide. JAMES WILFRED COOK and OSCAR LISLE BRADY (T., 1920, **117**, 750—753).

α-Aminophenyl-α-naphthylmethane. I. SERGIO BERLINGOZZI (*Gazzetta*, 1920, **50**, i, 215—221).—By reducing the two stereoisomeric oximes of phenyl α-naphthyl ketone by means of zinc and hydrochloric acid, Poccianti (A., 1915, i, 822) obtained aminophenyl-α-naphthylmethane hydrochloride, which agrees in properties with the hydrochloride prepared by Busch and Leefhelm (A., 1908, i, 152) from magnesium α-naphthyl bromide and hydrobenzamide. The latter authors give m. p. 121° for the corresponding free base, whereas the present author finds m. p. 56—59° for the base derived from Poccianti's hydrochloride. In the formation of the latter, the Beckmann transformation may possibly result in the change $OH\cdot N:CPh\cdot C_{10}H_7 \rightarrow C_6H_5\cdot CO\cdot NH\cdot C_{10}H_7$, so that the base would then have the formula $C_{10}H_7\cdot NH\cdot CH_2Ph$ instead of $C_{10}H_7\cdot CHPh\cdot NH_2$. That such change does not occur and that the base is actually a primary amine is shown by the facts that: (1) the same base is obtained when the oxime is reduced by means of sodium amalgam in acetic acid solution, (2) the action of nitrous acid converts the base into the corresponding alcohol, phenyl-α-naphthylcarbinol, (3) the base readily yields the corresponding *p*-hydroxybenzylidene derivative when treated with *p*-hydroxybenzaldehyde, and (4) benzoyl-α-naphthylamine,

$$C_{10}H_7\cdot NHBz,$$

is not reduced by sodium amalgam.

α-Aminophenyl-α-naphthylmethane, $C_{10}H_7\cdot CHPh\cdot NH_2$, forms rosettes of long, colourless, prismatic crystals, m. p. 56—59°, and its *acetate*, shining, white scales, m. p. 119°. The p-*hydroxybenzylidene* derivative, $C_{10}H_7\cdot CHPh\cdot N:CH\cdot C_6H_4\cdot OH$, crystallises in tufts of minute, acicular crystals, m. p. 235°. T. H. P.

The Preparation of Picric Acid. Influence of the Degree of Sulphonation of the Phenol on the Yields of Trinitrophenol. MAURICE M. DOLL (*Bull. Soc. chim.*, 1920, [iv], **27**, 370—374).—Other things being equal, the yield of trinitrophenol increases regularly with the degree of sulphonation of the phenol. W. G.

Identification of Acids. V. *p*-Halogenophenacyl Esters. W. LEE JUDEFIND and E. EMMET REID (*J. Amer. Chem. Soc.*, 1920, **42**, 1043—1055).—Certain of the phenacyl esters previously described (A., 1919, i, 157) are oils or solids of low melting point. It is now shown that derivatives with a convenient range of melting points are, in general, easily obtained from *p*-halogenophenacyl bromides. The esters of aspartic, maleic, racemic, tartaric, and mucic acids derived from *p*-bromo- and *p*-chloro-phenacyl bromides decomposed without melting, whilst the salts of linoleic,

eic, oxalic, monochloroacetic, trichloroacetic, and formic acids did ot react. A liquid ester was obtained from α-hydroxybutyric id, and gallic acid gave only a small quantity of an unsatisctory product. p-*Iodophenacyl bromide* (ω-*bromo*-p-*iodoacetoenone*), $C_6H_4I·CO·CH_2Br$, yellow crystals, m. p. 113·5°, is tained by brominating *p*-iodoacetophenone. p-*Bromophenacyl cohol*, $C_6H_4Br·CO·CH_2·OH$, m. p. 136·6°, and p-*iodophenacyl cohol*, m. p. 152°, were obtained from the acetates by the action barium carbonate. The following esters were prepared (the mperatures indicating melting points):

p-*Chlorophenacyl acetate*, 67·2°; *aconitate*, 169°; *benzoate*, 8·6°; *ethylglycollate*, 94·4°; *succinate*, 197·5°; *thiocyanate*, 35·2°; *tricarballylate*, 125·6°.

p-*Bromophenacyl acetate*, 85°; *aconitate*, 186°; *anisate*, 152°; *nzoate*, 119°; *butyrate*, 63·2°; iso*butyrate*, 76·8°; *decoate*, 66°; *oate*, 71·6°; *octoate*, 65·5°; *cinnamate*, 145·6°; *citrate*, 148°; *ucate*, 61°; *ethylglycollate*, 104·8°; *glycollate*, 138°; *hippurate*, 51°; *β-phenylpropionate*, 104°; *lactate*, 112·8°; *laevulate*, 84°; *argarate*, 78·2°; *palmitate*, 81·5°; *phenylacetate*, 89°; *propionate*, °; *pyromucate*, 138·5°; *salicylate*, 140°; *sebacate*, 147°; *sorbate*, !9°; *stearate*, 78·5°; *succinate*, 211°; *thiocyanate*, 146·5°; *toluate*, 56·9°; m-*toluate*, 108°; p-*toluate*, 153°; *tricarballylate*, 38·2°; *valerate*, 63·6°; iso*valerate*, 68°.

p-*Iodophenacyl acetate*, 114°; *benzoate*, 126·5°; *butyrate*, 81·4°; *obutyrate*, 109·2°; *decoate*, 80°; *hexoate*, 81·5°; *octoate*, 77°; *ovalerate*, 78·8°; *erucate*, 73·8°; *lactate*, 139·8°; *margarate*, 88·8°; *lmitate*, 90°; *propionate*, 94·9°; *stearate*, 90·5°; *valerate*, 78·6°.

J. K.

Polymerisation in Ethereal Solution by means of Ferric hloride. Seventh Polymeride of Anethole. E. Puxeddu (*Gazzetta*, 1920, **50**, i, 149—154. Compare A., 1913, i, 460; 1916, 806).—Addition of ethereal ferric chloride solution to an ethereal lution of anethole results in the immediate precipitation of a hite substance; fractional distillation of the latter under duced pressure yielding a new polymeride, the seventh known, of ıethole. The author and Marica (A., 1916, i, 807) consider that even such isomeric polymerides are possible, although Orndorff ıd Morton (A., 1900, i, 289) maintain that phenols containing a openylic chain are able to exist in only two isomeric forms. The ıthor has prepared in the pure state the *p*-butenyl- and *p*-*iso*entenyl-anisoles described by Moureu and Chauvet (A., 1897, 403), and has studied their bromides and polymerides.

The seventh *polymeride* of anethole, $(C_{10}H_{12}O)_2$, forms prismatic ystals, m. p. 132°; owing to lack of material, its molecular weight as not determined.

p-Butenylanisole has b. p. 245—248°, and yields a dibromide, hich was not analysed, and, when treated with ethereal ferric ıloride, a dense, oily polymeride.

p-*iso*Pentenylanisole forms a colourless, faintly opalescent liquid,

b. p. 248—252°, *n* 1·54, with the odour of aniseed. The bromide (*not analysed*) *forms long, slender needles, m. p.* 93—95°, and the polymeride a dense, gummy mass. T. H. P.

o-Anisyltellurium Compounds. KARL LEDERER (*Ber.*, 1920 **53**, [*B*], 712—716. Compare A., 1917, i, 134; this vol., i, 40).—Di-*o*-anisyl telluride has been prepared by the action of magnesium *o-anisyl bromide on tellurium dibromide; it is purified by con*version into the crystalline dibromide, and reduction of the latter *with magnesium methyl iodide.*

Di-o-anisyl telluride, $Te(C_6H_4{\cdot}OMe)_2$, is a colourless, crystalline *substance, m. p.* 73—74°, b. p. 248—251°/30 *mm.*, which give rise to the following *di-o-anisyltelluronium* compounds in the usual way: *dichloride*, microscopic rods, m. p. 184—185° after softening at 182°; *dibromide*, small, monoclinic platelets, m. p. 195—196 after softening at 192°; *di-iodide, shining, metallic, iodine-coloured* needles, m. p. 199—200° after softening at 198°; *oxide*,

$$TeO(C_6H_4{\cdot}OMe)_2,$$

needles, m. p. 205—206°; *methiodide*, small rods, m. p. 124—125° It also forms *additive compounds with mercuric haloids, as follows iodide*, $Te(C_6H_4{\cdot}OMe)_2,HgI_2$, yellow crystals, m. p. 80—81° after softening at 79°; *bromide*, yellow crystals, m. p. about 84° after softening at 70°; *chloride*, obtained as an oil, which, after solidification, has m. p. 143—144°, and after recrystallisation has m. p. 156—157° (decomp.) after softening at 150°. H. W.

Relationship between Chemical Constitution and Physiological Action in Local Anæsthetics. I. Homologues of Procaine. OLIVER KAMM (*J. Amer. Chem. Soc.*, 1920, **42**, 1030-1033).—γ-*Diethylaminopropyl* p-*nitrobenzoate hydrochloride*, from *p*-nitrobenzoyl chloride and γ-diethylaminopropyl alcohol, m. p. 189—190°, *on reduction with tin and hydrochloric acid gives* γ-*diethylaminopropyl* p-*aminobenzoate*, m. p. 69° (*hydrochloride* needles, *m. p.* 164°), which is structurally similar to cocaine, and in physiological action is intermediate between this drug and procaine (novocaine). It is slightly more toxic, but considerably more effective as a surface anæsthetic than the latter. γ-*Diethylaminopropyl* m-*nitrobenzoate hydrochloride*, m. p. 139—140°, yields γ-*diethylaminopropyl* m-*aminobenzoate*, a colourless oil, which solidifies only at a low temperature (*hydrochloride*, m. p. 151°). J. K.

The Constitution of Acylanthranils. GUSTAV HELLER (*Ber.*, 1920, **53**, [*B*], 731—732).—*A further contribution to the discussion* on this subject (compare Heller and Lauth, this vol., i, 18 Schröter, this vol., i, 333). The author maintains his original views, and points out that the properties of the crystalline additive products of hydrazine and lactones differ considerably from those of the substances formed from hydrazine and acylanthranils particularly from the point of relative stability. H. W.

β-Halogenoethylaminobenzoic Esters. J. ALTWEGG and J. LANDRIVON (U.S. Pat. 1334641).—*Ethyl* p-*β-chloroethylaminobenzoate*, $CH_2Cl\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2Et$, crystals, m. p. 69°, b. p. 183°/3 mm., is obtained by adding a solution of the corresponding hydroxy-compound (20 parts) in dry benzene (15 parts) to a mixture of phosphorus pentachloride (20 parts) and dry benzene (25 parts), heating the mixture on the water-bath, evaporating the benzene and phosphoryl chloride, and distilling the residue under reduced pressure. Dimethylaniline and thionyl chloride may be used instead of benzene and phosphorus pentachloride; in this case, the product of the reaction is treated with warm water, whereby dimethylaniline hydrochloride dissolves and the ester separates in granules. Other esters may be prepared similarly. They are useful as local anæsthetics. CHEMICAL ABSTRACTS.

β-Alkylaminoethylaminobenzoic Alkyl Esters. J. ALTWEGG and J. LANDRIVON (U.S. Pat. 1334642).—*Ethyl* p-*β-diethylaminoethylaminobenzoate*, $NEt_2\cdot CH_2\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2Et$, an oil (hydrochloride, white needles, m. p. 156°), is obtained by heating a mixture of diethylamine (2 mols.) and ethyl *p*-β-chloroethylaminobenzoate (1 mol.) in a closed vessel for several hours at 100°, and treating the cooled, crystalline mass with water to dissolve diethylamine hydrochloride. The corresponding *butyl* ester has b. p. 213—214°/6 mm., and forms a *hydrochloride*, m. p. 127°. *Butyl* p-*β-methylaminoethylaminobenzoate*, b. p. 214°/6 mm., forms a hydrochloride, m. p. 141°. CHEMICAL ABSTRACTS.

Mechanism of the Reaction between Ketens and the Grignard Reagent. HENRY GILMAN and L. C. HECKERT (*J. Amer. Chem. Soc.*, 1920, **42**, 1010—1014).—Hitherto, all the reactions of the ketens have been attributed to initial addition to the ethylenic linking, but, on the other hand, no case is known in which the Grignard reagent combines directly with such linkings. By direct benzoylation of the initial product of the reaction between diphenyl keten and magnesium phenyl bromide, triphenylvinyl benzoate, $CPh_2{:}CPh\cdot O\cdot COPh$, was obtained, showing that addition of the Grignard reagent had taken place at the carbonyl group. J. K.

Iodination of the Phenoxyacetic Acids. EFISIO MAMELI, EVARISTO GAMBETTA, and GUIDO RIMINI (*Gazzetta*, 1920, **50**, i, 166—186).—Of the various methods tried for the iodination of phenoxyacetic acid and some of its substituted derivatives, the action of iodine in presence of iodic acid in chloroform solution is found to give the best results. The acids employed gave the following melting points, some of which differ slightly from those found in the literature: phenoxyacetic acid, 99—100°; 2-methoxyphenoxyacetic acid, 123—125°; 3-methyl-6-*iso*propylphenoxyacetic acid, 147—148°; α-naphthoxyacetic acid, 190°; β-naphthoxyacetic acid, 156°.

p-*Iodophenoxyacetic acid*, $C_6H_4I\cdot O\cdot CH_2\cdot CO_2H$, obtained by

iodinating phenoxyacetic acid, and also by the action of chloroacetic acid on *p*-iodophenol, crystallises in shining, colourless, odourless scales, m. p. 155—156°; at first it appears tasteless, but a persistent, sweet taste gradually develops. On nitration, it yields 4-iodo-3-nitrophenol. The *potassium*, *calcium* (+ $2H_2O$), *silver*, and *copper* (+ $2H_2O$) salts were prepared and analysed. The *ethyl ester*, $C_{10}H_{11}O_3I$, forms colourless, tasteless, rhombohedral plates, m. p. 62—63°, with a pronounced fruity odour. The *amide*, $C_8H_8O_2NI$, crystallises in silky, white needles, m. p. 165—166°.

5-*Iodo-2-methoxyphenoxyacetic acid*, $OMe{\cdot}C_6H_3I{\cdot}O{\cdot}CH_2{\cdot}CO_2H$, prepared by iodinating 2-methoxyphenoxyacetic acid, and also by the action of chloroacetic acid on 5-iodo-2-methoxyphenol, forms slender, white, odourless, tasteless needles, m. p. 155°. By cold concentrated sulphuric acid it is coloured first violet and then brown, and afterwards charred; the sulphuric acid solution colours chloroform violet, and emits iodine vapour when heated. Similar behaviour is shown by the yellowish-brown solution obtained with concentrated nitric acid. The *potassium* and *silver* salts were prepared and analysed.

4-*Iodo-2-methoxyphenoxyacetic acid*, obtained from 4-iodo-2-methoxyphenol and chloroacetic acid, crystallises in white, nacreous scales, m. p. 83—84°.

4-*Iodo-3-methyl-6-*iso*propylphenoxyacetic acid*,

$$C_6H_2MePr^{\beta}I{\cdot}O{\cdot}CH_2{\cdot}CO_2H,$$

prepared by iodination of 3-methyl-6-*iso*propylphenoxyacetic acid in *iso*amyl alcohol, and also by the action of chloroacetic acid on 4-iodo-3-methyl-6-*iso*propylphenol, crystallises in small, white, colourless, tasteless needles, m. p. 126—127°, and towards sulphuric and nitric acids behaves similarly to 5-iodo-2-methoxyphenoxyacetic acid. Its *potassium* and *silver* salts were prepared and analysed.

1-*Iodo-β-naphthoxyacetic acid*, $C_{10}H_6I{\cdot}O{\cdot}CH_2{\cdot}CO_2H$, prepared by iodination of β-naphthoxyacetic acid, and also by the interaction of chloroacetic acid and 1-iodo-β-naphthol, forms thin, white, odourless plates, m. p. 170—171°. It becomes pale yellow at 138° and pink at 145°, the colour deepening as the melting point is approached; at 203—210° it decomposes, with emission of violet vapour. Concentrated sulphuric acid decomposes it, with evolution of violet vapour, the acid assuming a brown colour with green reflexion. In cold concentrated nitric acid it is insoluble, but the hot acid dissolves it, giving a ruby-red liquid and violet vapours. The *potassium* and *silver* salts were prepared and analysed.

Iodo-α-naphthoxyacetic acid, $C_{10}H_6I{\cdot}O{\cdot}CH_2{\cdot}CO_2H$, prepared by iodination of α-naphthoxyacetic acid, forms slender, pink, odourless crystals, m. p. 168—170°, and decomposes, with evolution of iodine vapour, at 195°. It colours concentrated sulphuric acid violet-pink, and liberates iodine when treated with boiling concentrated nitric acid. No suitable iodo-derivative of α-naphthol being known, the position of the iodine in this acid could not be established. The *potassium* and *silver* salts were prepared and analysed.

T. H. P.

The Behaviour of Optically Active Esters on Hydrolysis. ALEX. MCKENZIE and HENRY WREN (T., 1920, **117**, 680—690).

Case of Isomerism in the Series of Aromatic α-Ketonic Acids. H. GAULT and R. WEICK (*Compt. rend.*, 1920, **170**, 1392—1395).—Ethyl phenylpyruvate as prepared by Bougault (compare A., 1914, i, 839) and by Hemmerlé (compare A., 1915, i, 78) is a solid, m. p. 45° (the present authors find m. p. 51—52°). By the hydrolysis of ethyl cyanophenylpyruvate in alcoholic medium, and fractional distillation of the crude product, an isomeric ethyl phenylpyruvate is obtained as a liquid, b. p. 149°/15 mm., which will not solidify. This liquid isomeride gives a bisulphite compound, a semicarbazone, and a phenylhydrazone identical with those from the solid isomeride. It is shown that the solid isomeride is the unstable form, and that by slow distillation under reduced pressure it is converted into the stable liquid form, but the change is not reversible. The new method of preparation really gives a crude mixture of the two isomerides, which, during the fractional distillation, is entirely converted into the liquid form.

β-Hydroxy-α-phenylmaleimide was isolated as an intermediate product of the hydrolysis of ethyl cyanophenylpyruvate. W. G.

Synthesis of Bibasic Acids by the Action of Malonic Acid on Hydrols. Replacement of the Hydroxy-group by the Group $\cdot CH(CO_2H)_2$. R. FOSSE (*Ann. Chim.*, 1920, [ix], **13**, 154—183. Compare this vol., i, 390—396).—A more detailed account of work already published (compare A., 1906, i, 975; 1907, i, 414). W. G.

The Constitution of Some Dialkyl*cyclo*hexanones. R. CORNUBERT (*Compt. rend.*, 1920, **170**, 1259—1262. Compare A., 1914, i, 969).—A further study of the allyl derivatives obtained by the action of allyl iodide on *cyclo*hexanone and the three methyl*cyclo*hexanones in the presence of sodamide by means of the action of benzaldehyde (compare this vol., i, 390). The constitutions of these compounds are 1-methyl-1-allyl*cyclo*hexan-2-one, giving a *benzylidene* derivative, b. p. 211—212°/15 mm. (corr.); 1 : 1-diallyl*cyclo*hexan-2-one, giving a *benzylidene* derivative, b. p. 231—232°/18 mm. (corr.); 1-methyl-3 : 3-diallyl*cyclo*hexan-4-one with a *benzylidene* derivative, m. p. 71—71·5°; and 1-methyl-2 : 2(or 4 : 4)-diallyl*cyclo*hexane-3(or 5)-one with a *benzylidene* derivative, m. p. 45—48°. Similarly, other di- and tri-alkyl*cyclo*hexanones previously described (compare A., 1914, i, 951, 969) have the constitution 1-methyl-1-*n*-propyl*cyclo*hexan-2-one and 1-methyl-1 : 3-diallyl*cyclo*hexan-2-one. W. G.

Acidylketimines. CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1920, **170**, 1353—1356).—Organo-magnesium

derivatives of the type CRR′:N·MgBr, obtained by the condensation of nitriles, RCN, with magnesium alkyl bromides, R′MgBr, react with acid chlorides to give acidylketimines, thus:

CRR′:N·MgBr + R″COCl = CRR′:N·COR″ + MgBrCl.

In this way, the authors have prepared *acetylphenylethylketimine*, CPhEt:N·COMe, m. p. 126°; *butyrylphenylethylketimine*, m. p. 85·5°; *isovalerylphenylethylketimine*, m. p. 117°; *benzoylphenylethylketimine*, m. p. 165°; *acetylphenylisobutylketimine*, m. p. 134°; and *benzoylphenylisobutylketimine*, m. p. 160°.

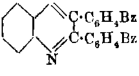
All these acidylketimines are hydrolysed by dilute mineral acids to give a ketone, an acid, and an ammonium salt,

CPhEt:N·COMe + $2H_2O$ + HCl = COPhEt + $CH_3·CO_2H$ + NH_4Cl.

When hydrolysed by alkalis, they give the ketone, the alkali salt of the organic acid, and ammonia. W. G.

The Stereoisomeric Forms of Benzoylphenylacetylene Di-iodide. CHARLES DUFRAISSE (*Compt. rend.*, 1920, **170**, 1262—1264. Compare A., 1914, i, 845).—Nef (compare A., 1900, i, 20) obtained only one di-iodide by the action of iodine on benzoylphenylacetylene. By suitably modifying Nef's process, the author has obtained two stereoisomeric di-iodides. The substance *A*, m. p. 155—156°, is the one described by Nef. The *di-iodide*, *B*, occurs in two distinct crystalline forms, B_a and B_β. B_a is converted into B_β when heated at its m. p., 82°; B_β has m. p. 84—85°, and is converted into B_a by rapid cooling or rapid evaporation of its alcoholic solution. W. G.

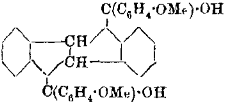
The Diphensuccindene Series. II. 2:2′-Dibenzoylbenzil and its Derivatives. K. BRAND and H. LUDWIG (*Ber.*, 1920, **53**, [*B*], 809—814).—The constitution assigned previously to the brown hydrocarbon, 9:12-diphenyldiphensuccindadiene (A., 1912, i, 960), is confirmed by the observation that it is oxidised by chromic acid in hot glacial acetic acid solution, with the production of two molecules of *o*-benzoylbenzoic acid from each molecule of the hydrocarbon. If, however, the oxidation is carried out in cold solution, 2:2′-*dibenzoylbenzil*, $C_6H_4Bz·CO·CO·C_6H_4Bz$, yellow crystals, m. p. 188°, is obtained. The latter slowly condenses with *o*-phenylenediamine in boiling glacial acetic acid solution to yield 2:3-*di*(*o*-*benzoylphenyl*)-*quinoxaline* (annexed formula), colourless, silky crystals, m. p. 237—238°. 2:2′-*Di*-*p*-*toluoylbenzil*, yellow crystals, m. p. 191°, is similarly formed from 9:12-di-*p*-tolyldiphensuccindadiene. H. W.



The Diphensuccindene Series. III. Coloured Phenol Ethers of the Diphensuccindene Series. K. BRAND and F. W. HOFFMANN (*Ber.*, 1920, **53**, [*B*], 815—821. Compare A., 1912, i, 960, and preceding abstract).—The action of magnesium *o*- and *p*-anisyl bromides on diphensuccindan-9:12-dione has been investigated, and a series of derivatives have been prepared which

are closely similar to the phenyl and *p*-tolyl compounds described previously.

8 : 12 - *Dihydroxy*-8 : 12-*di* - o- *anisyldiphensuccindane* (annexed formula) forms colourless, transparent needles, m. p. 207·5°, and is converted by a boiling mixture of glacial acetic and formic acids into 9 : 12 - *di-o-anisyldiphensuccindadiene*, reddish-brown needles, m. p. 247°. The latter is oxidised by a warm solution of chromic acid in glacial acetic acid to 2 : 2′-*di-o-anisoylbenzil*, $OMe·C_6H_4·CO·C_6H_4·CO·CO·C_6H_4·CO·C_6H_4·OMe$, pale yellow needles, m. p. 244°, which condenses with *o*-phenylenediamine to yield 2 : 3-*di*[o-*anisoylphenyl*]-*quinoxaline*, almost colourless needles, m. p. 250°.



9 : 12-*Dihydroxy*-9 : 12-*di*-p-*anisyldiphensuccindane*, colourless, transparent needles, m. p. 230°, is readily dehydrated to 9 : 12-*di*-p-*anisyldiphensuccindadiene*, brown needles, m. p. 242°. (When the Grignard reagent is prepared from *p*-anisyl iodide, the diene is sometimes the only isolable substance.) It is converted by gentle oxidation with chromic acid in glacial acetic acid into *di*-p-*anisoylbenzil*, yellow needles, m. p. 214°, whilst more drastic oxidation converts it into 2-*p*-anisoylbenzoic acid, m. p. 138° (the literature records m. p. 142—143°). The benzil condenses with o-phenylenediamine to yield 2 : 3-*di*(p-*anisoylphenyl*)-*quinoxaline*, almost colourless needles, m. p. 251°. H. W.

Constitution of Enols. IV. Enolisation of 2-Monoacylindane-1 : 3-diones. Johannes Scheiber and Georg Hopfer (*Ber.*, 1920, **53**, [*B*], 697—706).—The enolisation of monoacylindanediones may occur in such a manner as to yield products of the formula (*i*) $C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{CO}>C·OR$ or

$$(ii)\ C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C:CR·OH.$$

The authors have therefore investigated the behaviour of ethyl 1 : 3-diketohydrindene-2-carboxylate, 2-acetyl- and 2-benzoyl-1 : 3-diketohydrindenes towards ozone, and in each case find that enolisation occurs, at any rate to some extent, so as to give rise to substances of the second formula.

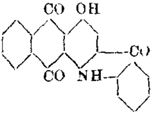
The main products of the action of ozone on a solution of ethyl 1 : 3-diketohydrindene-2-carboxylate in carbon tetrachloride at $-20°$ are phthalic acid and ethyl glyoxalate, which can only be derived from an enol of type (i); at the same time, considerable quantities of carbon dioxide are formed, the bulk of which is attributable to the decomposition of ethyl hydrogen carbonate, whilst smaller quantities arise from the oxidation of triketohydrindene to phthalic acid, thus indicating that enolisation also occurs in such a manner as to yield type (ii). Ozonisation of 1 : 3-diketo-

2-acetylhydrindene must produce either phthalic acid and methyl glyoxal or triketohydrindene and acetic acid, according as enolisation gives rise to type (i) or (ii); actually, the latter substances are produced, and although the absence of enolisation to type (i) is not definitely excluded, it appears certain that at least 95% of the transformed substance belongs to type (ii). It is, however, remarkable that about 60% of the original material remains unaffected by ozone, although titration by Meyer's method indicates the presence of more than 90% of enol. The products obtained from 1:3-diketo-2-benzoylhydrindene are phthalic acid, a strongly reducing substance, which is probably phenylglyoxal, benzoic acid, and carbon dioxide; triketohydrindene cannot be detected, and is probably destroyed by oxidation. Only about 80% of the original substance enters into action, although the Meyer titration method indicates an almost exclusively enolic form. It appears that about 40% of the enolised portion belongs to type (ii). H. W.

Some Properties of Benzanthrone. ARTHUR GEORGE PERKIN (*T.*, *1920*, **117**, *696—708*).

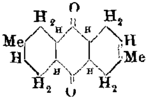
4-Chloro-1-hydroxyanthraquinone. FRITZ ULLMANN and ACHILLE CONZETTI (*Ber.*, 1920, **53**, [*B*], 826—837).—1-Hydroxyanthraquinone is conveniently prepared by the diazotisation of a solution of 1-aminoanthraquinone in concentrated sulphuric acid, and is transformed by sulphuryl chloride in the presence of nitrobenzene at 100° into *4-chloro-1-hydroxyanthraquinone*, which, when obtained in this manner, can only be freed with difficulty from small amounts of dichlorohydroxyanthraquinone; if the chlorination is effected in the presence of a little iodine, 2:4-*dichloro-1-hydroxyanthraquinone*, shining, yellow needles, m. p. 242°, is obtained. The constitution of the substances is deduced from their synthesis in the following manner: (i) phthalic anhydride is condensed with *p*-chlorophenol in acetylene tetrachloride solution in the presence of aluminium chloride to *5-chloro-2-hydroxy-o-benzoylbenzoic acid*, $HO·C_6H_3Cl·CO·C_6H_4·CO_2H$, colourless leaflets, m. p. 202° after softening slightly at 196°, which is transformed by sulphuric acid monohydrate into 4-chloro-1-hydroxyanthraquinone, small, yellow crystals, m. p. 193° (corr.); (ii) a molten mixture of phthalic anhydride and 2:4-dichlorophenol is converted by aluminium chloride into *3:5-dichloro-2-hydroxy-o-benzoylbenzoic acid*, colourless leaflets, m. p. 204° (corr.), which is then transformed into 2:4-dichloro-1-hydroxyanthraquinone, m. p. 242°, in the usual manner. 4-Chloro-1-hydroxyanthraquinone is readily converted into 1:4-dichloroanthraquinone, m. p. 187°, by phosphorus pentachloride at 155—160° if care is taken to remove the phosphoryl chloride as rapidly as it is formed; under similar conditions, 2:4-dichloro-1-hydroxyanthraquinone gives 1:2:4-trichloroanthraquinone, m. p. 185·5° (corr.). The α-chloro-atoms of the hydroxyanthraquinones may be replaced by the hydroxyl group by treatment with boric and sulphuric acids at 156—160°, thereby yielding

1:4-*dihydroxyanthraquinone*, m. p. 198° (corr.), and 2-chloro-1:4-dihydroxyanthraquinone, dark red, shining needles, m. p. 239°, respectively. 4-Chloro-1-hydroxyanthraquinone is transformed by *p*-toluenesulphonamide in amyl-alcoholic solution in the presence of copper and potassium acetates into 1-*hydroxy*-4-p-*toluenesulphonamidoanthraquinone*, orange-yellow needles, m. p. 197°, which is hydrolysed by concentrated sulphuric acid to 4-amino-1-hydroxyanthraquinone, dark red, metallic needles, m. p. 215° (Wacker, A., 1903, i, 132, gives 207—208°). 2-*Chloro*-1-*hydroxy*-4-p-*toluenesulphonamidoanthraquinone*, pale red needles, m. p. 198°, and 2-*chloro*-4-*amino*-1-*hydroxyanthraquinone*, wine-red needles, m. p. 236°, are similarly derived from 2:4-dichloro-1-hydroxyanthraquinone. 1-*Hydroxy*-4-*anilinoanthraquinone*, dark violet, shining leaflets, m. p. 161°, is obtained from the monochloroanthraquinone, aniline, potassium acetate, and a trace of copper acetate. The similarly prepared 2-*chloro*-1-*hydroxy*-4-*anilinoanthraquinone* crystallises in dark violet needles, m. p. 195°. N[1-*Hydroxyanthraquinonyl*-4]-*anthranilic acid* is most conveniently prepared by boiling a solution of 4-chloro-1-hydroxyanthraquinone and anthranilic acid in amyl alcohol with anhydrous potassium acetate in the presence of copper acetate and copper powder; it forms bluish-violet, shining needles, m. p. 272° (corr.; decomp.). The substance is not transformed into 4-*hydroxyanthraquinone*-2 : 1-*acridone* (annexed formula) by sulphuric acid or phosphoric oxide, but the conversion may be effected by the action of acetic anhydride in the presence of pyridine, and subsequent treatment of the acetyl *derivative* so formed with *p*-toluenesulphonyl chloride; the acridone crystallises in shining, blue leaflets, m. p. 321°, and gives blue shades on cotton from a wine-red vat.



H. W.

Condensations at Double Bonds. I. Condensation of Isoprene with *p*-Benzoquinone. H. VON EULER and K. O. JOSEPHSON (*Ber.*, 1920, **53**, [*B*], 822—826).—When isoprene is heated with one-sixth to one-seventh of its weight of *p*-benzoquinone for five to six hours at temperatures ranging from 120° to 180°, it readily yields a *product*, m. p. 234°, to which the annexed formula is assigned (in which the 2:7-position of the two methyl groups is uncertain). The mechanism of the reaction is therefore closely analogous to that of the condensation of isoprene to dimethyl*cyclo*octadiene. The substance readily unites with bromine in glacial acetic acid solution, yielding the *tetrabromide*, $C_{16}H_{20}O_2Br_4$, m. p. 210° (corr.; decomp.). With hydroxylamine, it gives a *dioxime*, which commences to decompose above 200°, and probably also a *monoxime*. Preliminary experiments show that it is readily oxidised by per-

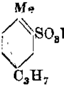


manganate, and thereby undergoes very extensive decomposition. Reduction by hydrogen in ethereal solution in the presence of platinum-black appears to lead to the formation of a substance, $C_{16}H_{26}O_2$. H. W.

The Camphane Series. XXXVIII. The Cyanohydrazone of Camphorquinone. MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE (T., 1920, **117**, 753—761).

Pulegonesulphonic Acid. The Behaviour of Sabinol and Sabinene towards Sulphurous Acid and Thujone. OTTO WALLACH [with G. REGGELIN, F. RIESENER, and HEUBNER] (*Nachr. Ges. Wiss. Göttingen*, 1919, 321—336; from *Chem. Zentr.*, 1920, i, 671—672).—Pulegonesulphonic acid is obtained as an almost colourless syrup when an alcoholic solution of pulegone is saturated with sulphur dioxide and preserved in a closed vessel for several days at 20°; it forms well-crystallised salts, which obstinately retain water (the *magnesium, zinc, lead, barium, calcium, ammonium*, and *piperidine* compounds are described). Such of them as do not contain poisonous metals are devoid of physiological activity.

Purified sabinol is similarly converted into its *sulphonic acid* at 0°. (In addition, small quantities of an insoluble, amorphous *substance*, m. p. 213—215°, which appears to be an ester, and of a neutral *compound*, woolly needles, m. p. 147—148°, are obtained.) The acid has m. p. 98—99°, becomes discoloured, and finally liquefies on exposure to air; it behaves like an unsaturated substance towards bromine or potassium permanganate. Its constitution has not been definitely elucidated, but its conversion by



potassium hydroxide solution (1:1) into an alcohol, which, after reduction and oxidation, yields thujone, b. p. 199—200°, indicates the annexed formula. On the other hand, an acid of this constitution should yield α-thujoketonic acid when cautiously oxidised by potassium permanganate, but this product has not been obtained so far.

Sabinol is converted by hydrogenation in the presence of palladium chloride into a hydrocarbon, b. p. 161—163°, D^{21} 0·795, n_D 1·4375, and an alcohol, b. p. 206—208°, D^{20} 0·9090, n_D 1·4576, the latter being the main product. It is oxidised by the calculated quantity of chromic acid in glacial acetic acid solution to *l*-thujone, b. p. 203—205°, D^{20} 0·907, n_D 1·4507, $[\alpha]_D$ −30·62° in 16·1% methyl-alcoholic solution. Potassium permanganate converts it into α-thujoketonic acid. The unusually high specific rotation indicates the possible presence of a third isomeride of thujone.

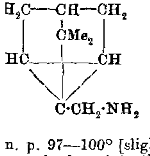
Oils containing thujone become strongly acidic when preserved, mainly owing to the formation of α-thujoketonic acid. H. W.

Homocamphor. ARTHUR LAPWORTH and FRANK ALBERT ROYLE (T., 1920, **117**, 743—750).

Preparation and Properties of isoAmylcamphor and Some of its Derivatives. FÉLIX MARTIN (*J. Pharm. Chim.*, 1920, [vii], **21**, 417—425).—A mixture of *iso*amylcamphor and *iso*amylcamphol is obtained by dissolving one atomic equivalent of sodium in an excess of *iso*amyl alcohol, adding one molecular equivalent of camphor, and heating the mixture at 140° for fifteen hours under a reflux apparatus. The mixture of the two substances when oxidised with permanganate in benzene solution yields iso*amylcamphor*, a yellow, odourless oil, b. p. 165°/33 mm., D_4^{15} 0·9272, $[\alpha]_D^{15}$ + 59° (in alcohol), + 38·4° (in benzene). Reduction with sodium in alcoholic solution converts the mixture into *isoamylcamphol*, m. p. 25—28°, b. p. 190°/61 mm., D_4^0 0·9611, $[\alpha]_D^{15}$ + 17° (in alcohol). iso*Amylcamphyl acetate*, a colourless liquid, b. p. 169°/30 mm., D_4^{15} 0·9402, $[\alpha]_D^{15}$ + 7·24° (in alcohol), is obtained by acetylating *iso*amylcamphol. W. P. S.

Tricyclene. P. LIPP (*Ber.*, 1920, **53**, [*B*], 769—781).—It has been suggested by Semmler that tricyclene is an intermediate product in the conversion of borneol or *iso*borneol into camphene. Since, however, the formulation of this substance has been doubted by Meerwein (A., 1914, i, 850), although the objections he raises have been partly removed by Ruziska (A., 1918, i, 398), the author has endeavoured to prepare the hydrocarbon from a similarly constituted substance, and for this purpose has chosen tricyclenic [dehydrocamphenylic] acid, the formula of which has been established with practical certainty by Komppa and Hintikka (A., 1908, i, 852), and by Komppa (A., 1911, i, 642). He has thereby succeeded in establishing definitely the constitution of the hydrocarbon and in showing that it is readily converted by sodium hydrogen sulphate at 160° into camphene, but not by zinc chloride in benzene solution. Tricyclene may therefore be an intermediate product in the formation of camphene from borneol, but not from *iso*borneol.

An ethereal solution of tricyclenyl chloride is converted by gaseous ammonia into tricyclenamide, shining, rhombic leaflets, m. p. 117—118° (corr.) (Komppa and Hintikka, *loc. cit.*, give 114·5°), which is transformed by phosphorus trichloride into *tricyclenylonitrile*, b. p. 100—102° (corr.)/12 mm., m. p. 65—70°. The latter is reduced by sodium and alcohol to ω-*aminotricyclene* (annexed formula), colourless, paraffin-like mass, which melts with the warmth of the hand and has b. p. *ca.* 100—101°/27 mm. (the *hydrochloride*, colourless leaflets, which does not melt below 266°, and the *carbonate*, slender needles, m. p. 97—100° [slight decomp.], are described). Attempts to convert the base into the corresponding primary alcohol by means of sodium nitrite and hydrochloric acid were unsuccessful, an oily, heterogeneous product being obtained, which owed its formation to rupture of the ring system. The ease with which this occurs is

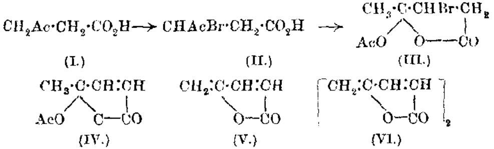


further illustrated by the conversion of ω-aminotricyclene hydrochloride into camphenilanaldehyde and ammonia by warming for a short time with fuming hydrochloric acid.

A more successful series of experiments has tricyclenic acid for its starting point. The latter is converted by methyl alcohol and sulphuric acid into *methyl tricyclenate*, m. p. 38°, b. p. 99° (corr.)/14 mm., $D_4^{12\cdot6}$ 1·0255, $n_D^{12\cdot6}$ 1·46953, which is reduced by sodium and alcohol to *tricyclol*, colourless needles, m. p. 111—112° (corr.), b. p. 141°/71 mm. (*phenylurethane*, long, slender needles, m. p. 92—93° [corr.]; *tricyclyl chloride*, b. p. 85—88°/14·5 mm., 81—82·5°/11 mm.). The alcohol is converted by chromic acid in acetic acid solution into *tricyclal*, b. p. 113—115°/31 mm., the smooth conversion of which into tricyclenic acid shows that the carbon skeleton has been unchanged up to this point (*tricyclalsemicarbazone* forms small, matt needles, m. p. 219—220° [decomp.]). *Tricyclalazine*, prisms or cubes, m. p. 171—172° (corr.), is prepared by the action of hydrazine hydrate on the aldehyde, and is converted by an excess of hydrazine into the *monohydrazone*, which could not be obtained in the pure condition; the crude product was therefore directly heated at 180—195° with a solution of sodium in alcohol, whereby it was almost quantitatively transformed into tricyclene, mixed, however, with small quantities of an unsaturated hydrocarbon, probably camphene. The latter can be removed by treatment with potassium permanganate in glacial acetic acid solution, thus yielding ultimately pure tricyclene, b. p. 151·6—152° (corr.)/736 mm., m. p. 64—65°. The hydrocarbon is somewhat readily affected by potassium permanganate in warm glacial acetic acid solution, yielding tricyclenic acid and a carbonyl compound; the formation of the former shows that the hydrazone fission has occurred in the normal manner, and also that the same ring system is common to tricyclene and tricyclenic acid. H. W.

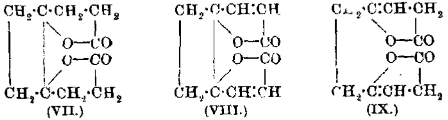
Croton Resin. R. BOEHM (*Arch. expt. Path. Pharm.*, 1915, **79**, 138—154).—The optical activity of croton oil is due to a resin which is dissolved in it. On removing the resin from the oil by extraction with methyl alcohol, the oil becomes inactive. The optical rotation of a croton oil may therefore serve as an indicator of its resin content. This resin has already been described by Dunstan and Boole (A., 1895, i, 680), but the author gives an improved method for its extraction. Croton resin is a practically colourless, light powder with no definite melting point. It becomes soft, but not liquid, at 80—90°. It is sparingly soluble in water and soluble in all proportions in organic solvents with the exception of light petroleums. The mean iodine value is 76·98. The rotation of various samples ranged from $[\alpha]_D$ +49·96° to +63·23°. Discordant results were obtained on analysis and molecular weight determinations of different samples; the formula $C_{36}H_{54}O$ and mol. wt. 627 are suggested with reservation. An attempt to throw some light on the constitution of the compound failed. The pharmacological activity of the resin is similar to that observed previously with croton oil. S. S. Z.

Synthesis and Constitution of Anemonin. Y. ASAHINA and A. FUJITA (*J. Pharm. Soc. Japan*, 1920, **455**, 1).—The chief results of this investigation may be summarised as follows: The sharp, oily substance volatile with steam obtained from *Ranunculus scleratus* L., consists in the main of the parent substance of anemonin, and has been given the name *protoanemonin*, which under spontaneous union of 2 mols. passes into anemonin. The synthesis of protoanemonin (V) was effected in the following manner: Lævulic acid (I) is converted into β-bromolævulic acid (II), and the latter acetylated; the resulting acetyl derivative (III) in anhydrous ether is digested with anhydrous sodium acetate, the acetylacetoacrylic acid (IV) doubtless formed thereby yielding on distillation a strongly vesicant oil protoanemonin, which on stirring quickly changes into anemonin (VI), m. p. 158°. Anemonin



(I.) (II.) (III.) (IV.) (V.) (VI.)

was also prepared, but in poorer yield, by similar treatment of dibromoangelicalactone. Owing to the unpleasant physiological action of ranunkel oil, an attempt was made to convert it into dihydroanemonin (IX). The latter could not be isolated in a pure condition, but was characterised by means of its semicarbazone, m. p. 185°, identical with the semicarbazone of lævulic acid, $CH_3{\cdot}C(:N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$. Anemonin is thus shown to be a dimeric product of protoanemonin and is constituted in accordance with the formula (VIII), whilst tetrahydroanemonin and dihydroanemonin have the constitutions represented by (VII) and (IX) respectively.



(VII.) (VIII.) (IX.)

CHEMICAL ABSTRACTS.

Colloid Chemical Studies on the Acids of Hop Bitters. H. LÜERS and A. BAUMANN (*Kolloid Zeitsch.*, 1920, **26**, 202—212).—The properties of the acid of hop bitters, both in aqueous solution and in wort, have been investigated by means of the change in surface tension which this substance brings about. Humulon (α-hop

bitter acid) exists in the form of an hydrosol as a typical colloid-disperse system with a negative charge and in character intermediate between a suspensoid and an emulsoid. It is coagulated by heavy metals and is further dispersed by salts of the alkali metals. The presence of anions changes the surface tension of the solutions in the order chlorion $<$ thiocyanate ion $<$ iodion $<$ sulphion $<$ tartration. The humulon hydrosol changes its dispersity spontaneously *with time in the sense that the particles become larger* with a simultaneous increase in the surface tension. In acid solutions, the surface tension is smallest, the bitter taste least pronounced and the turbidity greatest, whilst in alkaline solution the reverse is the case. Emulsions exercise a dispersing action on humulon hydrosol; this is particularly the case with gelatin, which differs from the other emulsoids in causing a large reduction of *the surface tension of solutions of the humulon hydrosol.* Hand in hand with the change in the dispersity, a very marked stabilising of the sol occurs. Humulon is strongly adsorbed by charcoal from aqueous solution, but less strongly from solutions of sodium potassium tartrate. With decreasing dispersion, the adsorption of humulon increases. The concentration of the sol and the surface tension of the solution follow a parabolic equation of the same form as the adsorption law. The *power of humulon to form a* stable foam is in keeping with its power of reducing surface tension and its adsorption. The changes which occur in humulon *on boiling are considered in* connexion with the processes occurring in brewing. J. F. S.

Hyptolide, a Bitter Principle of Hyptis pectinata, Poit. K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], **1**, 327—337). —The leaves of this Labiate are extracted with 95% alcohol; an equal volume of water is added, and after filtering off the chlorophyll, the filtrate is concentrated until there crystallises *hyptolide*, $C_{18}H_{26}O_8$, colourless needles, m. p. 88·5°, $[\alpha]_D^{27}$ +6·75°. Yield, 2% of the leaves. The substance dissolves in 50 parts of boiling water and readily in most organic solvents; it distils unchanged under *reduced pressure. It contains a lactone group (hence the name)* and three acetyl groups. After oxidation with silver oxide in alkaline solution and hydrolysis, four equivalents of acetic acid are liberated, the fourth one resulting apparently from the oxidation of a terminal group $-CH(OH)\cdot CH_3$. This group is eliminated to some extent as acetone by steam distillation with 10% sodium hydroxide, when at the same time an additional carboxyl group is generated. The mechanism of this reaction is represented as follows, where the group R contains the preformed carboxyl of the lactone,

$$OH\cdot CRR'\cdot CH(OH)\cdot CH(OH)\cdot CHMe\cdot OH \rightarrow CRR'{:}C(OH)\cdot CH{:}CMe\cdot OH \rightarrow CHRR'\cdot CO\cdot CH_2\cdot COMe \rightarrow CHRR'\cdot CO_2H + COMe_2.$$

Reduction in alcoholic solution with hydrogen and palladium

chloride introduces six atoms of hydrogen, transforming the compound $C_{10}H_{14}Me(OAc)_3<\begin{matrix}CO\\|\\O\end{matrix}$ into an oil,

$$OH\cdot C_{10}H_{16}Me(OAc)_3\cdot CH_2\cdot OH.$$

The latter contains three acetyl groups, but no lactone grouping; on boiling with acetic anhydride, one of the hydroxyl groups is eliminated as water, the other is acetylated; the resulting tetra-acetyl derivative is an oil.

Oxidation of hexahydrohyptolide with potassium permanganate in alkaline solution gives one-third of its weight as a mixture of acids; from water there first crystallises a dibasic *acid*, $C_9H_{16}O_4$, needles, m. p. 130—131°, soluble in 180 parts of water at 26°, dissociation constant, $4\cdot 2\times 10^{-5}$. The residue from the mother liquor of this acid was esterified, the ester was distilled, and after hydrolysis yielded αα-dimethylglutaric acid, $C_7H_{12}O_4$. Hence it is concluded that the acid $C_9H_{16}O_4$ must be either αββ- or αα′α′-trimethyladipic. The latter acid is known and melts at 115°, so that the acid from hexahydrohyptolide is considered to be identical with the former.

Oxidation of hexahydrohyptolide with nitric acid (D 1·2) on the water bath also yields a small quantity of this supposed αββ-trimethyladipic acid, together with succinic acid. The following formula for the hexahydro-derivative is arrived at:

$$OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe_2\cdot CMe(OH)\cdot[CH(OAc)]_3\cdot CH_3;$$

and for the hyptolide itself:

$$\begin{matrix}CH\cdot CMe_2\\ \|\\ CH\cdot CO\cdot O\end{matrix}>CMe\cdot[CH(OAc)]_3\cdot CH_3.$$

G. B.

Reduction of Elsholtzia Ketone [Elsholtzione]. MICHIZO ASANO (*J. Pharm. Soc. Japan*, 1919, **454**, 999—1006).—Elsholtzione, $CH_2Pr^{\beta}\cdot CO\cdot C<\begin{matrix}CMe\cdot CH\\ \quad\ \ \|\\ O\text{——}CH\end{matrix}$ (A., 1915, i, 430), the reduction of which by the Clemensen and the Sabatier and Senderens methods has been unsuccessfully attempted by Asahina and his co-workers, is reduced by heating in a sealed tube with sodium ethoxide and hydrazine sulphate to *3-methyl-2-isoamylfuran*, b. p. 172°/atm. or 78—79°/25 mm., D_4^{23} 0·8814, n_D^{19} 1·45178. This substance is not identical with dihydroperillen (b. p. 182°, D_4^{22} 0·8852, n_D^{22} 1·45762); consequently, the positions of the two substituents in perillen, $CH_2{:}CMe\cdot CH_2\cdot CH_2\cdot C_4H_2MeO$, are still undetermined. CHEMICAL ABSTRACTS.

8-Hydroxy-2 : 3-quinoxanthone. HARRY FITZGIBBON DEAN and MAXIMILIAN NIERENSTEIN (T., 1920, **117**, 802—806).

An Alkaloid in the Toxin of Bufo vulgaris. HANS HANDOVSKY (*Arch. Exp. Path. Pharm.*, 1920, **86**, 138—159).—The aqueous extract of the toxin from *Bufo vulgaris* after being freed from the colloid it contains was treated with chloroform in order to

remove the bufotalin, and was precipitated with phosphotungstic acid in the presence of sulphuric acid. The precipitate was again brought into solution by various methods which are described, and extracted with ether. Some anhydrous oxalic acid was then added to the dehydrated ethereal extract, when the new alkaloid, *bufotenine*, crystallised as its oxalate, $(C_6H_9ON)_2,C_2H_2O_4$. The author adduces evidence for the provisional constitution

$$\begin{matrix} CHMe\cdot CO \\ | \\ CH{=\!=}CH \end{matrix} > NMe.$$

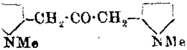
S. S. Z.

Cinchona Alkaloids. III. Nitro- and Amino-sulphonic Acids, Nitro- and Amino-bases of some Hydrogenated Cinchona Alkaloids. G. Giemsa and J. Halberkann (*Ber.*, 1920, **53**, [*B*], 732—750. Compare A., 1919, i, 342).—The hydrogenated alkaloids under investigation are smoothly converted by concentrated sulphuric acid and the calculated quantity of nitric acid (*D* 1·4) or nitrate into crystalline nitro-sulphonic acids, which are easily hydrolysed by warm 25% hydrochloric acid, and thus particularly adapted to the preparations of the pure nitro-bases. They are readily reduced to the corresponding amino-sulphonic acids by ferrous sulphate in the presence of alkali, and this behaviour is of the greater importance, since the amino-bases are not readily sulphonated. The amines themselves are smoothly obtained by hydrolysis of the aminosulphonic acids. The introduction of the nitro-group is found to increase the negative specific rotation of the compounds, whilst the amino-group displaces the rotation in the dextro-direction: the latter tendency is strengthened by the introduction of the sulphonic radicle to such an extent that aminohydroquininesulphonic acid is dextrorotatory.

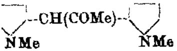
The following individual compounds are described: 5-*Nitrohydrocupreinesulphonic acid*, $C_{19}H_{23}O_7N_3S$, coarse, golden-yellow prisms, which gradually become green on exposure to sunlight and darken at 205°, and completely decompose, without melting, above 245°. 5-*Nitrohydroquininesulphonic acid*, anhydrous, yellow needles, which are sensitive to light and decompose above about 250°. $[\alpha]_D^{20}$ −172·4° (in alcohol), −186·7° (in alcohol and 10% aqueous ammonia). 5-*Nitroethylhydrocupreinesulphonic acid*, yellow, prismatic needles, sensitive to light and decomposing above about 270°. *Nitrohydrocinchoninesulphonic acid*, yellow, microscopic platelets or cubes or prismatic rods ($+H_2O$), thin, rectangular plates ($+2H_2O$), m. p. (anhydrous) 236° (decomp.). *Nitrohydrocinchonidinesulphonic acid*, pale yellow, four-sided platelets, decomposing above *ca.* 270°. *Nitrohydrocupreine*, $C_{19}H_{23}O_4N_3$ (from the sulphonic acid and hydrochloric acid [D 1·126]), coarse, red crystals, m. p. 192° (decomp.) after darkening at about 180°. 5-*Nitrohydroquinine*, pale yellow, anhydrous crystals, which are alkaline towards litmus, m. p. 210—212° (decomp.) (the *monosulphate*, golden-yellow prisms [$+15H_2O$] and the *disulphate*, yellow, amorphous powder [$+2H_2O$], are described). 5-*Nitroethylhydrocupreine*, almost colourless, anhydrous leaflets, m. p. 221—223° (decomp.), $[\alpha]_D^{20}$ −250·4° in alcohol, −222·1° in chloroform. *Nitrohydro-*

nchonine, coarse, pale yellow, anhydrous plates, m. p. 234—235° lecomp.), $[\alpha]_D^{20}+163°$ in alcohol, $+161·8°$ in chloroform. *Nitro-ydrocinchonidine*, yellow, crystalline powder, m. p. 148° lecomp.), $[\alpha]_D^{20}-65·2°$ in alcohol, $-60·4°$ in chloroform. *Aminohydroquininesulphonic acid*, yellow, anhydrous needles, . p. about 227° (decomp.) after darkening at about 218°, · coarse, yellow prisms ($+3H_2O$), $[\alpha]_D^{20}+18·85°$ in absolute cohol, $+15·8°$ in a mixture of alcohol and aqueous ammonia (the *onosulphate*, reddish-brown needles [$+3H_2O$] or yellowish-red, norphous powder [$+H_2O$], is described). *5-Aminoethylhydro-upreinesulphonic acid*, pale yellow needles ($+H_2O$), which become ihydrous and intensely reddish-brown when preserved over ilphuric acid. *Aminohydrocinchoninesulphonic acid*, almost colour-ss, coarse, anhydrous needles, m. p. 276° (decomp.). *Aminohydro-nchonidinesulphonic acid*, practically colourless, anhydrous needles, m. p. 282° (decomp.). 5-Aminohydroquinine (by hydrolysis ' the aminosulphonic acid or reduction of the corresponding nitro-erivative by ferrous sulphate), yellow needles, m. p. 216—218°, $]_D^{20}-19·99°$ in absolute alcohol, $-120·9°$ in ether (the *sulphate*, ellowish-red crystals [$+5H_2O$], is described). 5-Aminoethylhydro-upreine, from the aminosulphonic acid or the corresponding nitro-mpound, m. p. 212°, $[\alpha]_D^{20}-16·98°$ in alcohol, $-123·8°$ in ether, entical with the base prepared previously (*loc. cit.*) from the zo-compound. *Aminohydrocinchonine*, yellow, prismatic plates or lourless needles, according to the solvent used for crystallisation, . p. 247°, $[\alpha]_D^{20}+204°$ in absolute alcohol. *Aminohydro-nchonidine*, colourless needles, m. p. 170°, to a yellow liquid, $]_D^{20}-80·7°$ in absolute alcohol. H. W.

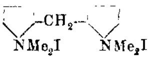
Hygrine Alkaloids. III. Constitution of Cuskhygrine. onversion of Cuskhygrine into Hygrine. KURT HESS and EINRICH FINK (*Ber.*, 1920, **53**, [*B*], 781—809. Compare A., 913, i, 1378; 1914, i, 199).—Cuskhygrine has been isolated by Liebermann from the liquid mixture of bases obtained in the preparation of cocaine, and on account of its empirical composition and its oxidation to hygric acid (1-methyl-yrrolidine-2-carboxylic acid) has been assigned the annexed



ormula, in which, however, the symmetrical arrangement and the resence of the second pyrrolidine ring cannot be regarded as roved. The authors now bring definite evidence to show the resence of the carbonyl group, but find that cuskhygrine does not ondense with benzaldehyde, oxalic ester, or amyl nitrite, and ence does not contain the active methylene group which the bove formula indicates. Further examination leads them to assign the constitution shown by the annexed formula to the base, the most important evidence for which is founded on the observations of Traube on the action of nitric oxide on ketones in the



presence of sodium ethoxide. Under these conditions, one molecule of cuskhygrine invariably absorbs six molecules of the gas. The primary additive product was too unstable to permit its isolation, but, on hydrolysis, yielded the sodium compound of methylenedi*iso*nitroamine, $CH_2(N_2O_2Na)_2$; the latter can only result from *the presence of a methyl group, and accounts for the absorption of* four molecules of nitric oxide. Since, according to Traube, a methylene group reacts more readily than the methyl radicle, it follows that such a group cannot be present in cuskhygrine, and that the absorption of the two remaining molecules of the gas is *due to the presence of a methine group. Further products of the* fission of cuskhygrine *iso*nitroamine are 1-methyl-2-pyrrolidylacetic acid and a non-homogeneous, basic oil, which, after hydrogenation and treatment with sodium methoxide and methyl iodide, gives a uniform biquaternary iodide (annexed formula), *thus affording convincing proof of* the presence of a second pyrrolidine ring. Additional evidence in favour of the newer formula is also provided by the isolation of two isomeric hydrazones, which is impossible if the constitution assigned by Liebermann be accepted.



Cuskhygrine, b. p. 169—170°/23 mm., is converted by hydroxylamine into the corresponding *oxime*, flat pyramids, m. p. 53—54°, which does not undergo the Beckmann transformation when treated with phosphorus pentachloride, glacial acetic–hydrochloric acids, or sulphuric acid. The *semicarbazone* is a non-crystalline syrup. *Cuskhygrine-α-hydrazone*, colourless, syrupy oil, which has a marked tendency towards polymerisation, b. p. 182—183°/14 mm., is obtained in quantitative yield by the action of hydrazine hydrate on an alcoholic solution of the base; in addition to this substance, *cuskhygrine-β-hydrazone*, b. p. 119—120°/15 mm., was obtained when (and only when) an old and somewhat decomposed specimen of hydrazine hydrate was used. The α-hydrazone is only converted by sodium ethoxide to a relatively small extent into the corresponding *amine*, b. p. *ca.* 125°/16 mm., which gives a *picrate*, long needles, m. p. 185°; the β-hydrazone, on the other hand, yielded a *product*, b. p. 95—99°/20 mm., the *picrate* of which was found to be identical with that of di-1-methyl-2-pyrrolidylmethane (see later).

The products of the action of nitric oxide on cuskhygrine, and subsequent hydrolysis of the primary compound, were isolated in the following manner: (i) Methylenedi*iso*nitroamine was identified as the crystalline barium salt, $CH_2O_4N_4Ba,3H_2O$, which was further characterised by conversion into the silver salt and the dimethyl ester, m. p. 134°. (ii) 1-Methyl-2-pyrrolidylacetic acid was converted into its *ethyl* ester, colourless oil with basic, aromatic odour, b. p. 89—90°/15 mm. (*picrate*, prisms, m. p. 113°; *methiodide*, coarse, prismatic needles, m. p. 105—106° after slight previous softening), and the latter was hydrolysed by aqueous barium hydroxide to 1-*methyl-2-pyrrolidylacetic acid*, colourless crystals, which are very susceptible to the action of air, m. p. 95° (the m. p. is

given with reserve, as a suitable solvent for recrystallisation of the acid has not been found). (iii) The basic constituents were separated into two fractions, of which that of higher b. p. consisted of unchanged cuskhygrine, whilst that of b. p. 90—98°/16 mm. was found to be composed of a mixture of bases, which could not be separated by distillation. It did not yield a crystalline picrate, and was therefore hydrogenated in the presence of colloidal platinum. The mixture of saturated bases, b. p. 99—109°/16 mm., yielded a picrate, which gradually became completely solid, and, after repeated crystallisation, gave a pure specimen of di-1-methyl-2-pyrrolidylmethane picrate, m. p. 203° (see above). The action of formaldehyde and formic acid on the hydrogenated bases (which thus consist of a mixture of partly demethylated and methylated di-1-methyl-2-pyrrolidylmethanes) did not give a homogeneous product, but a more successful result was obtained by exhaustive methylation with sodium methoxide and methyl iodide, whereby the 1 : 1′-*dimethiodide* of *di*-1-*methyl*-2-*pyrrolidylmethane* was prepared in cubic crystals, m. p. 200° after slight previous softening; it was further characterised by converting it, by means of silver chloride, into the *methochloride*, and transformation of the latter into the *aurichloride*, canary-yellow, microcrystalline powder, which decomposed at 260°.

When an ethereal solution of cuskhygrine is allowed to remain for a considerable time in contact with solid potassium hydroxide, the base undergoes a partial conversion into *r*-hygrine (the picrate of the latter has m. p. 149—150°, instead of 174° [corr.], after softening at 160°, as previously recorded), brown, viscous products being simultaneously formed. A similar change is observed when cuskhygrine is boiled for some time with aqueous-alcoholic potassium hydroxide solution. H. W.

Pelletierine and Methylpelletierine. GEORGES TANRET (*Compt. rend.*, 1920, **170**, 1118—1120).—The author reaffirms his results as to the properties of the two alkaloids, pelletierine and methylpelletierine, found in the bark of the pomegranate tree (compare A., 1880, 481), and refutes the statements of Hess and Eichel (compare A., 1917, i, 349; 1918, i, 33, 34) as to the non-existence of optically active forms of these alkaloids. Certain salts are described.

Pelletierine, $[\alpha]_D$ −31·1°, gives a *sulphate*, m. p. 133°, $[\alpha]_D$ −30·3°; a *hydrochloride*, m. p. 145°, $[\alpha]_D$ −41·2°; a *hydrobromide*, m. p. 137°, $[\alpha]_D$ −32·5°; a *nitrate*, m. p. 82—85°, $[\alpha]_D$ −34·8°; a *picrate*, m. p. 131—133°; a *platinichloride*, m. p. 214—216°; a *silicotungstate*; an *acetyl* derivative, b. p. 205—210°/40 mm., $[\alpha]_D$ +32·6°; a *benzoyl* derivative, $[\alpha]_D$ +18·7°; and a *semicarbazone hydrochloride*, m. p. 168—170°, $[\alpha]_D$ −10·8°. Pelletierine is very sensitive to heat and to acids and bases, rapidly losing its optical activity.

Methylpelletierine, b. p. 106—108°/45 mm., $[\alpha]_D$ +27·7°, and in aqueous solution +24·1°, gives a *hydrochloride*, m. p. 168—170°,

$[\alpha]_D$ +41·2°; a *hydrobromide*, m. p. 165—167°, $[\alpha]_D$ +33·5°; a *sulphate*, $[\alpha]_D$ +38°: a *picrate*, m. p. 157—159°; and a *platinichloride*, m. p. 206—208°. W. G.

The Chemical Isolation of Vitamines. C. N. MYERS and CARL VOEGTLIN (*J. Biol. Chem.*, 1920, **42**, 199—205).—Autolysed yeast filtrate is not a satisfactory product from which to attempt the isolation of the antineuritic vitamine. The active material is readily extracted from dried yeast by means of acidified methyl alcohol. From this fraction, an active, crystalline substance can be obtained by using Funk's silver acetate method, followed by mercuric sulphate precipitation. This substance becomes inactive on drying. The method eliminates purines, histidine, proteins, and albumoses. Stachydrine, trigonelline, and allied betaines show no antineuritic activity. J. C. D.

Constitution of the Organic Nitrogen Bases of Californian Petroleum. C. F. MABERY and L. G. WESSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1014—1030).—A re-examination of the basic constituents of Californian petroleum (A., 1900, i, 533) has shown them to consist mainly of alkylated quinolines (or *iso*quinolines), with a small proportion of hydrogenated derivatives or pyridine compounds. By refractionation, the material was divided into fractions boiling over intervals of 2—4° covering a range of 130—283°/50—90 mm. The analysis and mol.-wt. determination of one of these agreed with the formula of an alkylated quinoline, $C_{15}H_{19}N$, whilst from another an acid ferrocyanide, derived from the base, $C_{13}H_{15}N$ was obtained. All the fractions yield pyridine pentacarboxylic acid and a methylpyridinetetracarboxylic acid when boiled with potassium permanganate solution, and therefore contain at least three alkyl groups, of which the relatively simple nature is shown by the absence of propionic, or higher fatty, acid from the oxidation products. 3-Methylquinoline was obtained by distilling with lime the chromic acid oxidation product of one fraction of base. A medium fraction yielded a phthalone derivative by condensation with phthalic anhydride. The bases are unchanged by nitrous acid, but can be reduced to secondary bases, from which nitroso-derivatives are obtainable. Thus, a product, b. p. 208—210°/90 mm., $C_{14}H_{20}N$ or $C_{14}H_{21}N$, was obtained from a fraction $C_{14}H_{17}N$. Unsuccessful attempts were made to break down the pyridine ring of the benzoylated reduction product by means of phosphorus pentachloride. Definite picrates, platinichlorides, or double mercury salts could not be obtained from any fraction, probably because these, although representing a fairly satisfactory separation of the bases as regards molecular weight, are nevertheless mixtures containing small proportions of the other components previously mentioned. A lower fraction underwent sulphonation with fuming sulphuric acid, whilst a medium one was resistant to this agent. The action of bromine, iodine, hydriodic acid, and nitric acid is also described. J. K.

A New Series of Nitrogenous Compounds obtained from 'amphoroxalic Acid. PERCY CHORLEY and ARTHUR LAPWORTH [., *1920*, **117**, 728—742).

The Addition of 1 : 3-Diketones to Thiocarbimides. I. .cetylacetone and certain Aryl Thiocarbimides. DAVID E. 'ORRALL (*J. Amer. Chem. Soc.*, 1920, **42**, 1055—1061).—Acetyl-ɔetone, in the form of its sodium salt, reacts at the ordinary ɔmperature with thiocarbimides with formation of thioanilides. he acetyl group is removed from these compounds by solution in ɔld alkali hydroxide, and acidification at 0° after some hours. oth the resulting, and the original, thioanilides give the same roducts, and react very easily with phenylhydrazine and with ydroxylamine, phenylhydrazones and *iso*oxazoles being respectively 'oduced, with elimination of the sulphur atom. *Thiodiacetoacetyl-nilide*, $CH_3{\cdot}CO{\cdot}CH(CS{\cdot}NHPh){\cdot}CO{\cdot}CH_3$, yellow needles, m. p.)7—108°, and *thioacetoacetylanilide*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CS{\cdot}NHPh$, ɔllow plates, m. p. 63·5—64°, each give the phenylhydrazone of ɔioformanilide when treated with phenylhydrazine, and with ydroxylamine, *3-anilino-5-methylisooxazole*, $O<\begin{matrix}CMe{:}CH\\ N{=\!=}C{\cdot}NHPh\end{matrix}$, ɔedles, m. p. 111—112°. *Thiodiacetoacetyl-*p*-toluidide*,

$$CHAc_2{\cdot}CS{\cdot}NH{\cdot}C_6H_4Me,$$

'llow plates, m. p. 132—133°; *thioacetoacetyl-*p*-toluidide*, $H_2Ac{\cdot}CS{\cdot}NH{\cdot}C_6H_4Me$, yellow needles, m. p. 68—69°; 3-p-*tolu-ino-5-methyl*isooxazole, $O<\begin{matrix}CMe{:}CH\\ N{=\!=}C{\cdot}NH{\cdot}C_6H_4Me\end{matrix}$, needles, m. p. :2—124°; *thiodiacetoacetyl-*p*-bromoanilide*,

$$CHAc_2{\cdot}CS{\cdot}NH{\cdot}C_6H_4Br,$$

'edles, m. p. 137—139°; *thioacetoacetyl-*p*-bromoanilide*,

$$CH_2Ac{\cdot}CS{\cdot}NH{\cdot}C_6H_4Br,$$

. p. 110—111°; *3-*p*-bromoanilino-5-methylisooxazole*,

$$O<\begin{matrix}CMe{:}CH\\ N{=\!=}C{\cdot}NH{\cdot}C_6H_4Br\end{matrix},$$

ɔedles, m. p. 178—180°; *thiodiacetoacetyl-*m*-toluidide*, yellow ates, m. p. 124—125°; *thiodiacetoacetyl-*o*-toluidide*, yellow plates, . p. 126·5—128°. J. K.

Preparation of an Arylcarbamide Chloride. FARBWERKE ɔRM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 318237; additional D.R.-P. 241822; from *Chem. Zentr.*, 1920, ii. 691).—*p*-Nitro-ɔiline (in place of β-aminoanthraquinone) is treated with carbonyl loride until the amine hydrochloride has completely disappeared 'th the object of preparing p-*nitrophenylcarbamide chloride -nitrophenylcarbamyl chloride*]; the temperature is below that . which the latter is converted into the corresponding carbimide. 'hen carbonyl chloride is passed into a cooled suspension of nitroaniline in toluene, a mixture of *p*-nitrophenylcarbamyl loride and nitroaniline hydrochloride is first produced; at the dinary or slightly higher temperature, the latter is converted into

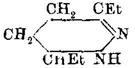
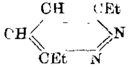
the carbamyl chloride, hydrogen chloride being evolved. The pure substance is a valuable intermediate product in the preparation of carbamide derivatives, and, for example, is quantitatively transformed by a solution of aniline in benzene into *p*-nitrodiphenylcarbamide. H. W.

Removal of Sulphur from Organic Compounds by means of Arsenic Trioxide. WALTHER HERZOG (*Zeitsch. angew. Chem.*, 1920, **33**, I, 140).—Organic compounds containing sulphur may be readily desulphurised by treatment with arsenic trioxide. The method is particularly suitable for the preparation of carbodiphenylimide from symmetrical diphenylthiocarbamide, which for the purpose is dissolved in xylene or other inert solvent and boiled with arsenic trioxide under reflux. C. A. M.

Orientation of the Nitro- and Arylazo-glyoxalines. Fission of the Glyoxalone Nucleus. ROBERT GEORGE FARGHER (T., 1920, **117**, 668—680).

Action of Hydrazine on the Acyclic 1 : 4-Diketones. E. E. BLAISE (*Compt. rend.*, 1920, **170**, 1324—1326).—Hydrazine acts on acetonylacetone in hydrochloric acid solution to give a *compound*, $C_{12}H_{20}N_4$, m. p. 52—53°, which is probably a dimeride of the dihydropyridazine expected.

In acetic acid solution hydrazine gives with *s*-dipropionylethane, *diethyltetrahydropyridazine* (I), b. p. 100°/15 mm., giving a *benzoyl* derivative, b. p. 210°/16 mm., and *diethylpyridazine* (II),

(I.)  (II.) 

b. p. 121—122°/15 mm., giving a *platinichloride*, m. p. 180—182°, and a *picrate*, m. p. 108—109°. W. G.

New Type of Diisonitroso-peroxides. E. J. VIRGIN (*Diss. Upsala*, 1914, pp. 63).—1:2:4:5-*Tetraketo*-3:6-*dibenzoyl*-4:5-*dihydropyridazine* [4 : 5-*diketo*-3 : 6-*dibenzoyl*-4 : 5-*dihydropyridazine* 1:2-*dioxide*] (A), NO:CBz·CO / NO:CBz·CO, red crystals exploding at 105—110° in a capillary tube, is obtained by warming αγδζ-tetraketo-αζ-diphenylhexane with nitrogen peroxide and ether at 25—27° for twenty minutes; it does not respond to the Liebermann nitroso-reaction. The mother liquors contain a small quantity of the substance O (see below). 1 : 5-*Dihydroxy*-2 : 4-*diketo*-3 : 6-*dibenzoyl*-1 : 4-*dihydropyridazine* [1 : 5-*dihydroxy*-4-*keto*-3 : 6-*dibenzoyl*-1 : 4-*dihydropyridazine* 2-*oxide*] (B), obtained from A by reduction in cold acetone with hydriodic acid (4 mols.) and a saturated solution of sulphur dioxide or with saturated hydrobromic acid, separates from acetone in pale yellow needles, m. p. 128° (decomp.), forms a *disodium* salt, develops a deep red coloration with ferric chloride in acetone solution, yields a *diacetyl* derivative, yellow needles, m. p. 160° (decomp.), and is reconverted into A by bromine

r nitrogen peroxide in ether or chloroform or by nitrous acid in ther. 1 : 5-*Dihydroxy-4-keto-3 : 6-dibenzoyl-1 : 4-dihydropyridazine* (C), obtained by keeping B with ice-cold acetic acid saturated with hydrogen iodide for two hours at the ordinary temperature and hen adding a saturated solution of sulphur dioxide, separates from lcohol in anhydrous, yellow crystals, m. p. 181—182°, or as a *ydrate*, yellow, microscopic needles and prisms, decomp. 125°; with ferric chloride in alcohol and acetone it develops an intense ed coloration, which changes through green to violet by the addiion of water. *ε-Chloro-β-oximino-αγδζ-tetraketo-αζ-diphenylhexane* D), obtained by treating an acetone solution of A with concenrated hydrochloric acid, crystallises from a mixture of ether and enzene in rhombic plates containing 1 mol. C_6H_6, develops a oloration with ferric chloride, and forms a *diacetyl* derivative, risms, m. p. 156—157°. 3-*Chloro-1 : 5-dihydroxy-4-keto-6-benzoyl-* : 4-*dihydropyridazine* (E), obtained together with its isomeride F below) by saturating a solution of B in 80% alcohol with hydrogen hloride at 0° and adding ether after concentration, forms yellow lades, m. p. 190° (decomp.). 6-*Chloro-1 : 5-dihydroxy-4-keto-3-enzoyl-1 : 4-dihydropyridazine* (F) separates from the alcoholic mother liquor in yellow crystals, m. p. 180°. 1 : 5-*Dihydroxy-4-eto-6-benzoyl-1 : 4-dihydropyridazine* (G), obtained by treating E ith hydriodic acid, forms yellowish-brown plates, m. p. 245° decomp.). 4 : 5-*Dihydroxy-6-benzoylpyridazine* (H), yellowish-hite crystals, m. p. 239—240° (slight decomp.), is obtained from in a similar manner. 1 : 5-*Dihydroxy-4-keto-6-benzyl-1 : 4-diydropyridazine* (I), needles, m. p. 261° (decomp.), is obtained by arming G with a solution of hydrogen iodide in acetic acid; the mother liquor, after being neutralised, yields 4 : 5-*dihydroxy-6-enzylpyridazine* (J), m. p. 252—253° (decomp.), which can also e prepared from H, I, and K.

3-*Chloro-4 : 5-dihydroxy-6-benzoylpyridazine* (K), rectangular lates, m. p. 232—233°, is obtained by treating F for thirty minutes ith an acetic acid solution of hydrogen iodide. 4 : 5-*Dihydroxy--benzoyl-3-benzylpyridazine* (L), pale yellow, rectangular prisms, . p. 229—230° (*monoacetyl* derivative, yellow prisms, m. p. 89—190°), is obtained by boiling C with the same reagent. By eating C with this reagent in a sealed tube for five hours, 4 : 5-*diydroxy-3 : 6-dibenzylpyridazine* (M), plates, m. p. above 300° *monoacetyl* derivative, plates, m. p. 215°; *diacetyl* derivative, risms, m. p. 147°), is obtained. *βε-Dioximino-αγδζ-tetraketo-αζ-dihenylhexane* (N), obtained by boiling B with acetone, forms thin risms, m. p. 126° (decomp.), yields *oximinobenzoylacetic acid*, O_2H·CBz:NOH, irregular prisms, m. p. 130° (decomp.), by treatment with sulphuric acid and acetone, and is converted into A and small quantity of O by treatment with nitrogen peroxide in thereal solution; it forms a *diacetyl* derivative, yellow crystals, . p. 166°. By treatment with hydrogen chloride in acetic acid is converted into an *isomeride* (O), the *diacetyl* derivative of hich has m. p. 186—187°.

3 : 5-*Dibenzoyl*-1 : 2 : 4-*oxadiazole*, $CBz<\begin{matrix}N\cdot O\\ N:CBz\end{matrix}$, six-sided plates, m. p. 105°, obtained by keeping A in methyl-alcoholic solution for twenty-four hours, forms a *diphenylhydrazone*, yellow needles, m. p. 171—172°. *Ethyl* 1 : 2 ; 4 : 5-*tetraketo*-4 : 5-*dihydropyridazine*-3 : 6-*dicarboxylate* [*ethyl* 4 : 5-*diketo*-4 : 5-*dihydropyridazine*-3 : 6-*dicarboxylate* 1 : 2-*dioxide*], m. p. 70°, is obtained from ethyl ketipinate and nitrogen peroxide in ethereal solution at −15°.

The dioximino-peroxides of ethyl acetonedicarboxylate are discussed, and reasons for some types of its reactions are given, based on the behaviour of analogous compounds of A.

CHEMICAL ABSTRACTS.

Bistetrazole. E. OLIVERI-MANDALÀ (*Gazzetta*, 1920, **50**, i, 256—261. Compare A., 1913, i, 1398).—Bistetrazole exhibits great stability, and only by means of hot concentrated sulphuric acid or fused potassium hydroxide is its molecule profoundly decomposed. When treated with diazomethane in absolute ethereal solution, it yields, together with a small proportion of the dimethyl derivative, a compound which is isomeric with bistetrazole, but, unlike the latter, exhibits no acid characters; for this compound the structure $\begin{matrix}N:N\\ N:N\end{matrix}>CH\cdot CH<\begin{matrix}N:N\\ N:N\end{matrix}$ is tentatively proposed.

Whereas concentrated sulphuric acid exerts oxidising and hydrolysing actions on bistetrazole, thus: $C_2H_2N_8 + 2H_2O + O = 3N_2 + 2CO_2 + 2NH_3$, fused potassium hydroxide decomposes it with formation of potassium azide, apparently in accordance with the equation $C_2H_2N_8 \longrightarrow 2N_3H + C_2N_2$. This tendency to lose azoimide manifested generally by cyclic compounds containing the grouping ·N:N·NH·, is exhibited also by most compounds in which the triazo-group, $\cdot N<\begin{matrix}N\\ \|\\ N\end{matrix}$, occurs; only azides of the following structures undergo decomposition with elimination of a molecule of nitrogen: (1) $\cdot CO\cdot \dot{C}H\cdot N_3 \longrightarrow N_2 + \cdot CO\cdot \dot{C}:NH$, and (2) $:CH\cdot CO\cdot N_3 \longrightarrow N_2 + :CH\cdot CO\cdot N: \longrightarrow :CH\cdot N:CO$.

The cryoscopic behaviour of bistetrazole in aqueous solution confirms the marked ionisation of this compound indicated by conductivity measurements (*loc. cit.*). In freezing acetic acid the molecular weight is normal.

The *isomeride* of bistetrazole (see above) forms acicular aggregates of crystals, m. p. 98—99°, and is insoluble in alkali carbonate solution.

Dimethylbistetrazole, $C_2N_8Me_2$, forms crystals, m. p. 150—160° and yields nitrogen and methylamine when treated with concentrated alcoholic potassium hydroxide. The *sodium*, $C_2N_8Na_2$, *silver* $C_2N_8Ag_2$, *barium*, $C_2N_8Ba,3H_2O$, and *copper*, C_2N_8Cu, salts were prepared and analysed; the copper and mercury salts explode violently when heated.

T. H. P.

The Structure and Properties of the Compound obtained by the Thermal Decomposition of *o*-Methoxyphenyl Benzylidenehydrazinocarboxylate. OTTO DIELS and HEINRICH GRUBE (*Ber.*, 1920, **53**, [*B*], 854—863).—In a previous communication (A., 1914, i, 940) it has been shown that *o*-methoxyphenyl benzylidenehydrazinocarboxylate is smoothly decomposed, when heated, into guaiacol and a sparingly soluble, crystalline substance, $(C_8H_6ON_2)_x$; the constitution of the latter is now shown to be represented by the formula $CHPh:N\cdot N<\substack{CO\\CO}>N\cdot N:CHPh$.

The compound is decomposed by protracted heating with a mixture of glacial acetic and fuming hydrochloric acids into benzylideneurazine, $CHPh:N\cdot N<\substack{CO\cdot NH\\ | \\CO\cdot NH}$, long, colourless needles, m. p. 254°, which is further decomposed by water into benzaldehyde and urazine, m. p. 270°. These reactions, however, throw but little light on the constitution of the substance, since the products could be equally well derived from a di- or tri-polymeride, discrimination between which cannot be effected by determination of the molecular weight on account of the very slight solubility of the substance. More information is afforded by its milder fission by means of phenylhydrazine in the presence of dimethylaniline, which gives rise to the *compound*, $CHPh:N\cdot N<\substack{CO\\CO}>N\cdot NH_2$, colourless, crystalline powder, m. p. 254—255°, and phenylbenzylidenehydrazine. The presence of a free amino-group in the former is shown by its conversion into a *monoformyl* derivative, shining crystals, m. p. 278°, and a *diacetyl* compound, colourless, pearly leaflets, m. p. 269°, as well as by its condensation with furfuraldehyde and anisaldehyde with the formation of *derivatives*, $C_{14}H_{10}O_3N_4$, pale brown prisms, which decompose without melting at 251° after darkening at 247°, and $C_{17}H_{14}O_3N_4$, colourless crystals, m. p. 272—273°, to a reddish-brown liquid after becoming yellow at 268°. The close relationship of the amine to the parent substance is shown by its re-conversion into the latter when boiled with benzaldehyde in dimethylaniline solution in an atmosphere of carbon dioxide. The amine or its formyl derivative is converted by boiling aqueous potassium hydroxide solution into dibenzylidenecarbohydrazide, $CHPh:N\cdot NH\cdot CO\cdot NH\cdot N:CHPh$, which when obtained in this manner forms small, canary-yellow leaflets, m. p. 198°; when, however, the compound is prepared by mixing alcoholic solutions of carbohydrazide and benzaldehyde in the usual manner, it is obtained in colourless leaflets. The same *formate*, colourless, silky, needles, m. p. 189—190°, with yellow coloration after softening at 187°, is obtained by the action of formic acid on either variety, and this is converted by alkali or by heat (with evolution of formic acid) into the yellow modification. Precisely similar observations with the *acetate* are recorded. Crystallographically, the modifications are identical with one another, and they also show the same

melting point since the colourless passes into the yellow variety when heated. H. W.

Isomeric Phthalylhydrazides. FREDERICK DANIEL CHATTAWAY and WILLIAM TESH (T., 1920, **117**, 711—720).

Action of Benzyl Alcohol on Albumins and Ferments. J. JACOBSON (*Compt. rend. Soc. Biol.*, 1920, **83**, 255—256; from *Chem. Zentr.*, 1920, i, 783).—Benzyl alcohol precipitates egg-albumin and peptone even from solutions containing one part in a million, and the precipitates do not redissolve in distilled water. Benzyl alcohol has a retarding action towards pepsin, pancreatin, the rennet ferment, the souring of milk, and brewer's yeast. H. W.

Temperature Sensitiveness of Saccharase (Invertase). H. VON EULER and I. LAURIN (*Arkiv. Kem. Min. Geol.*, 1917, **7**, No. 24, 1—30. Compare following abstract).—The temperature-coefficient of inversion by saccharase from yeast has been determined in solution of acidity $P_H = 4{\cdot}5$. The constant A of Arrhenius's temperature formula is found to be 10500 ± 500 for the range 0° to 20°, and this can be taken as the inversion constant over this range. At temperatures 20° to 52°, a smaller value, 8800 ± 400, is obtained. The inactivation of yeast at the optimum acidity has been determined over the range 50° to 65°. Heating yeast for one hour at 59° reduces the activity of the saccharase by one half. The inactivation constant at this temperature is $k_c = 5 \times 10^{-3}$. For $P_H = 4{\cdot}5$, the Arrhenius formula applied to the inactivation gives a constant 101000. The inactivation of saccharase has been determined for $P_H = 3$, 4, 5, and 5·7 over the range 42° to 55°, and it is shown that the minimum temperature sensitiveness lies at acidities $P_H = 4$—5, that is, at the acidity of optimum enzyme activity. The Arrhenius constant is greatest in this region. The temperature sensitiveness of separated invertase is very little different from that in the yeast cells. The cell appear to exercise a slight protecting action, which allows the non separated invertase to be heated to about 1° higher than th separated product. The inactivation temperature constant is little greater for the separated invertase than for the non-separatec Invertase from bottom yeast has a smaller temperature sensitiv ness than that from top yeast. The difference amounts to abou 2°, that is, the invertase from bottom yeast can be heated 2° high than that from top yeast. The greater stability of bottom yea in comparison with top yeast is not due to the presence of a pr tecting substance in the former, because the addition of the liqu from bottom yeast to top yeast does not increase the stability this substance. J. F. S.

Influence of Temperature and Acidity on the Formati of Saccharase. H. VON EULER and O. SVANBERG (*Arkiv. Kem. M Geol.*, 1917, **7**, No. 23, 1—32).—The dependence of sacchara formation on the temperature and acidity has been investigate

It is shown that for yeast a well-defined temperature optimum for saccharase formation lies between 26° and 30°, and that at 35° no further formation takes place. The saccharase formation is strongly dependent on the acidity of the solution. The maximum formation occurs practically at the same point as the maximum activity of the enzyme. At a greater acidity than $P_H = 2$, a disturbance of the saccharase is noticed, but even at acidity $P_H = 6—7$ a strong enzyme formation occurs, which is about 90% of that observed under the best conditions of acidity. The saccharase content of fresh living yeast is not changed by ten hours' washing with water at 10°. J. F. S.

Diphenylarsenious Chloride and Cyanide. (Diphenylchloroarsine and Diphenylcyanoarsine.) GILBERT T. MORGAN and DUDLEY CLOETE VINING (T., 1920, **117**, 777—783).

Organo-derivatives of Bismuth. III. The Preparation of Derivatives of Quinquevalent Bismuth. FREDERICK CHALLENGER and ARCHIBALD EDWIN GODDARD (T., 1920, **117**, 762—773).

Physiological Chemistry.

Liquid for Determining Specific Gravity of Blood. H. HARTRIDGE (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxxxiii).—Lyle's golden syrup made up with water to D 1·080 is a good substitute for the usual glycerol solution. A few c.c. of formalin solution should be added as a preservative. J. C. D.

The Neutrality of the Blood. W. M. BAYLISS (*J. Physiol.*, 1920, **53**, 162—179).—Intravenous injection of acid in sufficient quantity to neutralise half the bicarbonate in the blood does not increase the hydrogen-ion concentration of the plasma. The chief mode of compensation is by increase in pulmonary ventilation, and consequent decrease of the carbon dioxide of the blood. Renal excretion of acid, and ammonia production in the liver, do not appreciably come into play in short experiments. Injected alkali is not so readily neutralised. The chief agent in this case appears to be excretion of alkaline urine. The proteins of the plasma play no perceptible part in the maintenance of neutrality between the limits of hydrogen-ion concentration possible in the living organism, namely, below 10^{-4} or above 10^{-10} normal. No evidence was obtained that either sodium bicarbonate, serum proteins, or both together convey carbon dioxide from the tissues to the lungs. Thus the only function of the sodium bicarbonate in the blood is to regulate the hydrogen-ion concentration, whilst under normal conditions the only function of the proteins is to give a colloidal osmotic pressure and a moderate degree of viscosity

to the plasma. A simple method of determining the hydrogen-ion concentration of blood by means of indicators is described.

J. C. D.

The Reaction and Carbon Dioxide-carrying Power of Blood. I. T. R. PARSONS (*J. Physiol.*, 1919, **53**, 42—59).—By mathematical calculation, it is determined that a system composed of carbon dioxide and one other weak acid with a fixed total amount of sodium distributed between them has a carbon dioxide dissociation curve identical with that of blood. The proteins of the blood constitute the second weak acid, which shares with carbon dioxide the available sodium. The whole of the combined carbon dioxide of the blood is in the form of bicarbonate, but the proteins present in the blood confer on it a property which pure bicarbonate solution does not possess, namely, that of forming an efficient carrier for carbon dioxide. In the blood, the "availability" of the sodium is regulated by the proteins in such a way that the carbon dioxide tends to be expelled at lower tensions, so that an efficient transport of gas is brought about.

CHEMICAL ABSTRACTS.

The Colloid-free Filtrate of Serum. A. R. CUSHNY (*J. Physiol.*, 1920, **53**, 391—398).—When serum is filtered through collodion membranes, the filtrate contains most of the crystalloid components in the same proportions as in the original serum. The only exceptions are calcium and possibly magnesium, which pass the filter in a lower concentration. Therefore the non-colloid constituents, other than these two elements, are in simple solution in serum, whilst part of the calcium and magnesium is probably in some form of combination with the proteins. J. C. D.

Metabolism of Carbohydrates. J. A. HEWITT and J. PRYDE (*Proc. Physiol. Soc.*, 1919; *J. Physiol.*, 1920, **53**, lxv; from *Physiol. Abstr.*, 1920, **5**, 79).—Experiments on the stereochemistry of certain carbohydrates in the alimentary canal indicate that the α- and β-forms of glucose are not present in a simply equilibrated aqueous solution. J. C. D.

Nitrogenous Equilibrium and Absence of Vitamines. A. DESGREZ and H. BIERRY (*Compt. rend.*, 1920, **170**, 1209—1211). —With a deficiency of vitamines, rats can be kept, for a certain time, in nitrogenous equilibrium for varying proportions of albumin, fats, and sugars, in a ration supplying sufficient energy. The minimum of albumin, fat, or sugar permissible is controlled by the chemical nature of the particular class of nutrient, and the ratio of the other two classes present. The minimum of nitrogenous nutrient necessary is reached when a sugar is present in sufficient amount in the ration. W. G.

Carrotinoids and Fat-soluble Vitamine. L. S. PALMER (*Science*, 1919, **50**, 1—2; from *Physiol. Abstr.*, 1920, **5**, 92).—The author disagrees with Steenbock's hypothesis as to the identity of carrotene and fat-soluble *A*. In many cases the relation breaks

down, and chickens have been raised to maturity on diets free from carotinoids. Further, certain oils (for example, cottonseed oil) are rich in carrotinoids, but are destitute of the fat-soluble vitamine. J. C. D.

The Behaviour of Basic Bismuth Nitrate towards Dilute Acids. P. W. K. Böckmann (*Arch. Exp. Path. Pharm.*, 1916, **80**, 140—146).—Experiments were instituted with the object of ascertaining whether basic bismuth nitrate is capable of neutralising acids. To nitric acid of known concentration, basic bismuth nitrate was added in excess and shaken for a couple of days at 18°. The bismuth, as well as the total acid content of the filtrate, was then estimated. On the assumption that the bismuth was present in the filtrate as the normal salt, the free acid was calculated by difference. The H-ion concentration of the above filtrates was also determined colorimetrically. From the results obtained, it was concluded that at an acidity similar to that which prevails in the stomach, basic bismuth nitrate does not possess any neutralising capacity. S. S. Z.

The Effect of Injection of Guanidine on the Creatine-content of Muscle. G. M. Wishart (*J. Physiol.*, 1920, **53**, 440—445).—Intravenous or subcutaneous injections of inorganic salts of guanidine cause an increase in the creatine content of muscles. The bearing of this observation on the theories of creatine formation is discussed. J. C. D.

The Formation of Adrenaline. F. Knoop (*Ber.*, 1920, **53**, [*B*], 716—718).—A further contribution to the controversy with regard to the mode of formation of adrenaline in the organism (compare Rosenmund and Dornsaft, this vol., i, 56, 327; Knoop, this vol., i, 161). H. W.

The Chemical Nature of the Bee's Poison. Ferdinand Flury (*Arch. Expt. Path. Pharm.*, 1920, **85**, 319—339).—The author carried out some investigations on the protein-free poison isolated by Langer from the poison sac of the bee. It was found that the principle was a base of complicated constitution. By means of digestive processes, a considerable fraction of a lipoid nature was obtained from it. The following were the products of hydrolysis with hydrochloric acid: (1) a ring compound of the indole series; (2) choline; (3) glycerol; (4) phosphoric acid; (5) palmitic acid; (6) a high molecular, non-crystallisable, unsaturated fatty acid; (7) a volatile fatty acid, presumably butyric acid; (8) and a nitrogen-free fraction. The latter fraction was found to be the pharmacologically active principle of the bee's poison. According to the method of isolation, it can be obtained either as a neutral compound sparingly soluble in water or as an acid soluble in water. The author expresses the opinion that the bee's poison in the natural secretion is present as a complex compound in combination with lecithin and a basic fraction.

S. S. Z.

The Nature of Excreted Arsenious and Arsenic Acids. GEORG JOACHIMOGLU (*Arch. Exp. Path. Pharm.*, 1916, **80**, 8—24). —The author shows that, on adding sodium arsenite to weakly alkaline urine and extracting it with alcohol, arsenic can be established both in the alcohol and in the residue. He therefore maintains that Salkowski is not justified in concluding that the arsenic found in an alcoholic extract of urine is of an organic nature. The author further criticises the various methods employed for the estimation of arsenic acid in the presence of arsenious acid, and considers that results obtained by such methods are not valid. He shows, on the other hand, that by means of electrolysis in alkaline solution, arsenious acid can be established with certainty in the presence of arsenic acid. Employing this method, he demonstrates that by injecting subcutaneously arsenic acid in dogs, at least 16% of the arsenic is excreted in the urine as arsenious acid. S. S. Z.

The Nature of Excreted Arsenious and Arsenic Acids. E. SALKOWSKI (*Arch. Exp. Path. Pharm.*, 1916, **80**, 231—235, *319—320*); G. JOACHIMOGLU (*ibid.*, 317—318).—Polemical in reference to Joachimoglu's criticisms (see preceding abstract) on Salkowski's earlier work. S. S. Z.

Influence of Adsorbent (especially Colloidal) Substances on the Separation of Uric Acid and its Salts from Supersaturated Solution. RUDOLF KOHLER (*Z. klin. Med.*, 1919, **88**, 14; *Zentr. Biochem. Biophys.*, **21**, 354—355).—In connexion with the work of Marc and with reference to the observations of Lichtwitz, the author has studied the influence of colloidal and other adsorbent substances on the separation of urates from supersaturated solutions. The conclusions deduced by Marc are essentially applicable to uric acid, but the retarding action is relatively small. This action applies only to the beginning of the separation and varies in a parallel manner with the adsorbability; its magnitude depends on the amount of substance which is added and the reciprocal value of the degree of supersaturation. The insignificance of this effect is explained by the fact that uric acid in solution (also its salts) has such a pronounced tendency towards supersaturation that the influence of the colloid has little relative value. Contrary to the view of Lichtwitz, the author does not, therefore, attach much importance to the action of colloids in holding crystalloids in solution in the urine and other fluids of animal origin. Colloids are superfluous, or at least of secondary importance, in so far as an explanation of the great solubility of uric acid in fluids of animal origin is concerned. CHEMICAL ABSTRACTS.

The Elimination of Taurine Administered to Man. CARL L. A. SCHMIDT and E. G. ALLEN (*J. Biol. Chem.*, 1920, **42**, 55—58).—Estimations of neutral sulphur and amino-acid nitrogen in the urine of an individual to whom had been given 10 grams of taurine per os show a close agreement, which indicates

that taurine is not eliminated as taurocarbamic acid (Salkowski, this Journ., 1872, 1033; 1874, 1129). Administration of taurine in large doses does not result in any marked changes in the excretion of urea and ammonia. J. C. D.

Excretion of Quinine in the Urine. M. NIERENSTEIN (Extract from Observations on Malaria, War Office, 1919, pp. 1—79).—See this vol., ii, 456.

Presence of True Mucin in Certain Urines. CH. O. GUILLAUMIN (*J. Pharm. Chim.*, 1920, [vii], **21**, 337—342).—The author has detected the presence of mucin in two samples of urine, both of which were distinctly acid in reaction. W. P. S.

Urochrome. J. MELLANBY and C. J. THOMAS (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, xcvii).—The pigment of urine is readily absorbed by animal charcoal of good quality. After washing the charcoal with warm water to remove traces of other urinary constituents, the pigment is removed with 50% alcohol containing 0·5% sodium hydroxide. After neutralisation with sulphuric acid, the fluid is concentrated, and the greater part of the sodium sulphate removed by crystallisation. From the aqueous solution, the pigment is precipitated by alcohol, washed with ether, and dried in a vacuum. The pigment may be purified further by repeated reprecipitation. It is a brown, amorphous powder, very soluble in water, but insoluble in the usual organic solvents. It shows no characteristic absorption bands. The aqueous solution slowly dialyses through parchment. No definite evidence of its metabolic significance has yet been obtained, but its excretion is roughly parallel with that of creatinine. J. C. D.

Physiological Radioactivity. H. ZWAARDEMAKER (*J. Physiol.*, 1920, **53**, 273—289. Compare A., 1917, i, 241).—In a large number of systems, the potassium ion may, as regards function, be replaced by all the other radioactive elements, the heavy ones as well as the light ones, provided the doses are equiradioactive.

When applied simultaneously, the substances emitting α-rays and those emitting β-rays are reciprocally antagonistic.

Potassium is (as a bearer of physiological radioactivity) for many cells a stimulus, which can restore and sustain function when it is brought in contact with the surface of the cells as a free, diffusible ion in the circulating fluid. A free radioactive radiation can take the place of potassium when previously the potassium is omitted from the circulation. J. C. D.

The Theory of Narcosis. E. VON KNAFFL-LENZ (*Arch. Exp. Path. Pharm.*, 1919, **84**, 66—88).—The surface tension against air and paraffin, and the partition coefficient in oil and water of the aqueous solution of various narcotics were determined at 10°, 20°, and 30°. The alterations in the surface tension, both against air and paraffin, at the different temperatures were not proportional

to the narcotic potency. A better agreement could be established between the partition coefficient and the narcotic potency, and the author therefore maintains that Traube's objections to the lipoid theory of narcosis are not justified. The influence of the vapour of volatile narcotics on jellies was also studied, and it was found, in contradistinction to Traube's results, that not only do the vapours not promote imbibition, but they produce the opposite effect. S. S. Z.

Relation between Chemical Constitution and Physiological Action in Local Anæsthetics. I. Homologues of Procaine. Oliver Kamm (*J. Amer. Chem. Soc.*, 1920, **42**, 1030—1033).—See this vol., i, 482.

Carbon Monoxide in Tobacco Smoke. H. Hartridge (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxxxii).—The positive results indicate the possibility of there being in a heavy smoker a condition of chronic carbon monoxide poisoning.
J. C. D.

Toxicity of Some Inorganic Substances to Paramœcium N. McCleland and R. A. Peters (*Proc. Physiol. Soc.*, 1919; *J. Physiol.*, 1919, **53**, xii).—There is a slight suggestion of a periodic rise and fall in toxicity with increase in molecular weight; thus vanadium–manganese–iron–nickel–cobalt–calcium, also silver–cadmium–tin–mercury–thallium(ic)–lead, seem to form such a series. The most toxic metals are bivalent. J. C. D.

Chemical Constitution and Physiological Action. The Toxicity of some Organic Metal Derivatives and some other Organic Substances. N. McCleland and R. A. Peters (*J. Physiol.*, 1919, **53**, xv).—The relation of chemical constitution to physiological action was tested by toxicity tests on *Paramoecia*. These preliminary experiments indicate that primary compounds are less toxic than secondary, that aliphatic compounds are less toxic than aromatic, and that arsenic compounds are less toxic than those of antimony. J. C. D.

Chemistry of Vegetable Physiology and Agriculture

Fermentation Characteristics of certain Pentose-destroying Bacteria. E. B. Fred, W. H. Peterson, and Audrey Davenport (*J. Biol. Chem.*, 1920, **42**, 175—189).—The average limit of growth in the yeast–water medium was approximately p_H 3·6 to 4·0 in the case of xylose, dextrose, galactose, sucrose, lævulose, and lactose. Mannitol was decomposed more slowly, and

gave a limit of about p_H 4·3. Acidity measurements and observation of the volume of gas liberated give no idea of the amount of carbohydrate fermented. The pentose sugars, arabinose and xylose, form on fermentation more than 20% of normal acid, divided into almost equal amounts of lactic acid and acetic acid. Rhamnose is not attacked by these organisms. The aldo-hexoses, dextrose and galactose, yield acetic acid, lactic acid, and ethyl alcohol, but the acid formation is small as compared with that observed in the fermentation of the pentose sugars. Mannose ferments more slowly than either dextrose or galactose, and yields nearly equal quantities of volatile and non-volatile acids. The ketone sugar, lævulose, is rapidly reduced by the pentose-fermenting organisms to form mannitol, volatile and non-volatile acids and carbon dioxide being formed at the same time. The chief disaccharides are all fermented, but never completely. Raffinose and melizitose are not attacked. A number of other substances were examined. Mannitol, glycerol, salicin, and xylan are slowly decomposed; æsculin, starch, inulin, cellulose, succinic, tartaric, and citric acids are not attacked, whilst pyruvic, lactic, and malic acids ferment, giving rise to closely related acids. J. C. D.

Sensitiveness of Yeast Fermentation to the P_H Value. H. VON EULER and S. HEINTZE (*Arkiv. Kem. Min. Geol.*, 1917, **7**, No. 21, 1—21).—The fermentation of sucrose and dextrose by yeast has been investigated at 28° in the presence of hydrochloric acid of varying concentrations with the object of ascertaining the dependence of the rate of fermentation on the P_H value of the solution. The P_H value was determined by Sörensen's indicator method, and the velocity of fermentation by direct measurement of the volume of carbon dioxide evolved in a given time by 200 yeast cells. All experiments were carried out at 28°. The maximum velocity of fermentation lies at $P_H = 5$, and this is also found when yeast-water or asparagine is added to the fermentation mixture, although in these cases the velocity is very much greater than in solutions which contain no absorbable nitrogen compound. The relative maximum velocities, expressed in c.c. of carbon dioxide evolved per hour, are: solutions without added nitrogen compounds, 75 c.c.; solutions with asparagine, 134 c.c.; solutions with yeast-water, 187 c.c. Oxalic acid and chromic acid in concentrations up to $0·025N$ do not act as yeast poisons, as has been frequently stated. In solutions of hydrochloric acid up to $0·01N$, the influence of the chlorine ions is unimportant, as also is the influence of the non-ionised molecules, but with weak organic acids the undissociated molecules play a considerable part. J. F. S.

Nitrogen of the Cyanogen Group in Fertilisation. R. PEROTTI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 206—210).—In presence of suitable nutrient substances, such as dextrose, potassium cyanide in concentrations of the order of 0·05% serves as nitrogenous nutriment for micro-organisms of various kinds.

T. H. P.

The Properties of Colloidal Systems. IV. Reversible Gelation in Living Protoplasm. W. M. BAYLISS (*Proc. Roy. Soc.*, 1920, [*B*], **91**, 196—201).—By means of suitable optical arrangements giving an intense dark-ground illumination, it is possible to see that the apparently clear pseudopodia of *Amoeba* are filled with numerous very minute particles in Brownian movement. This affords further evidence of the hydrosol nature of simple protoplasm. By suitable electrical stimulation, this sol can be reversibly changed into the gel state, the change being shown by the sudden cessation of the Brownian movement, which recommences when the stimulation is stopped. W. G.

Formation of Starch in Green Plants. C. RAVENNA (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 148—150).—Polemical. T. H. P.

Hydration Effects of Amino-compounds. D. T. MACDOUGAL and H. A. SPOEHR (*Proc. Soc. Expt. Biol. Med.*, 1919, **17**, 33—36; from *Physiol. Abstr.*, 1920, **5**, 102).—Experiments made on the swelling of agar and plant gums in solutions of amino-acids, both in the presence and absence of proteins, show that when the amino-acid is one which dissociates strongly, the swelling is less than in water. The reverse also holds. The concentration of hydrogen ions is not the only factor. J. C. D.

Distribution of certain Chemical Constants of Wood over its Proximate Constituents. W. H. DORE (*J. Ind. Eng. Chem.*, 1920, **12**, 472—476).—About one-half of the furfuraldehyde-yielding groups in redwood (*Sequoia sempervirens*) is associated with the cellulose, and only a small amount with the lignin. The acetic acid-yielding groups are associated with the cellulose and to a small extent with the lignin, whilst the methoxy-groups are associated entirely with the lignin. W. P. S.

Caltha palustris. E. POULSSON (*Arch. Exp. Path. Pharm.*, 1916, **80**, 173—183).—The chemical nature of the active principle of *Caltha palustris* (marsh marigold) was investigated. On distilling the aqueous extract of the fresh plant with sodium carbonate in steam, only ammonia was obtained. The author then had recourse to the potassium bismuth iodide method of precipitation employed by Jahns. The only base obtained in this way was choline. By precipitating the extract with phosphotungstic acid and examining the various fractions again, only choline was established. The author concludes that the traces of alkaloids and alkaloidal substances previously observed in extracts of *Caltha palustris* were choline. S. S. Z.

Fat-soluble Vitamine. VI. The Extractability of the Fat-soluble Vitamine from Carrots, Lucerne, and Yellow Corn by Fat Solvents. H. STEENBOCK and P. W. BOUTWELL [with MARIANA T. SELL and E. G. GROSS] (*J. Biol. Chem.*, 1920, **42**, 131—152).—Fat solvents, such as ether, chloroform, and

carbon disulphide, remove little or none of the fat-soluble accessory factor from carrots; alcohol and benzene, however, remove considerable amounts. Ether, benzene, and alcohol all removed a considerable proportion of the vitamine from lucerne. The superiority of alcohol as an extracting fluid is also demonstrated in the examination of yellow maize. The vitamine extracted from lucerne with alcohol resists hydrolysis with alcoholic potassium hydroxide in the cold, and can be recovered in the carrotene fraction of the unsaponifiable matter. The xanthophyll fraction is practically inactive. J. C. D.

Occurrence and Reactions of Anthocyanin Colouring Matters of the Beet-red Group. FERDINAND KRYZ (*Oesterr. Chem. Zeit.*, 1920, **23**, 55—56).—Members of the beet-red group of anthocyanins (Weigert, A., 1896, i, 387; Hilger and Mai, *ibid.*, 496) occur in the skins of fuchsia and cacti berries, and in the petals of scarlet cactus blooms. Fuchsia anthocyanin is insoluble in ether, chloroform, carbon disulphide, and amyl alcohol, but gives a carmine solution in acidified acetone or amyl alcohol. Potassium hydroxide or ammonia produces the characteristic yellow coloration, which becomes reddish with excess; organic acids or concentrated hydrochloric or sulphuric acid, a blackberry-red coloration, not destroyed by heat; nitric acid, a red coloration, yellow on warming; sodium carbonate, a dirty reddish-yellow coloration, bright yellow on warming; sodium hydrogen carbonate, a blue coloration, green on warming; mercuric chloride, sodium hydrogen sulphite, or bleaching powder, a light yellow coloration. Cactus bloom anthocyanin is soluble in water, methyl, ethyl, and acidified amyl alcohols, and in glycerol, but insoluble in ether, chloroform, and carbon disulphide. The details given in regard to the effect of reagents on it are very similar, except that the last-mentioned reagents cause decolorisation, slowly at the ordinary temperature, immediately on warming. The colouring matter from red beet also gives these reactions, and is soluble in cold acetone. Wing cactus blooms apparently contain two anthocyanins, because the reddish-yellow extract obtained with hot acetone exhibits slight differences from the above products, whilst the red aqueous solution of the residue gives all the above reactions. J. K.

Proteins from the Georgia Velvet Bean, Stizolobium Deeringianum. CARL O. JOHNS and HENRY C. WATERMAN (*J. Biol. Chem.*, 1920, **42**, 59—69).—The Georgia velvet bean contains 23·6% of protein ($N \times 6·25$). About 15% of protein is extracted by a 3% aqueous sodium chloride. By fractional precipitation with ammonium sulphate, and by subsequent purification of the fractions, two globulins, designated α and β, may be separated, in yields of of about 3 and 1·25% respectively. An albumin may also be isolated in yields of about 0·75%. When analysed by Van Slyke's method, the three proteins show marked differences. There is apparently no tryptophan in the β-globulin. J. C. D.

Exosmosis of Acid Principles and Sugars from the Orange. G. André (*Compt. rend.*, 1920, **170**, 1199—1201).—During exosmosis, the ratio of the citric acid to the total sugars, reducing and non-reducing, which have diffused out remains constant. Similarly, the ratio of sucrose to reducing sugars is fairly constant, but in considering this ratio it must be remembered that inversion of a portion of the sucrose occurs during exosmosis.

W. G.

The Proteins of Green Leaves. I. Spinach Leaves. Thomas B. Osborne and Alfred J. Wakeman [with Charles S. Leavenworth and Owen L. Nolan] (*J. Biol. Chem.*, 1920, **42**, 1—26).—By diluting the thoroughly ground leaves with one or two volumes of water and centrifugalising the extract at high speed, a solution of leaf proteins may be obtained. From this, impure protein substances may be precipitated by the addition of alcohol. This fraction is considerably purified from pigments and other substances by extraction with alcohol and ester, yielding a nearly colourless product containing about 14% of nitrogen, calculated on the ash free substance. At least 40% of the total nitrogen of spinach leaves is contained in colloidal protein; about one-third in substances which are soluble in water; and a comparatively small part in chlorophyll, phosphatides, and, presumably, nucleic acid. There are reasons for believing that certain of the constituents of the cell exist normally in the form of complexes. Examination of spinach leaves dried by warm air below 60° showed that their composition closely resembles that of the fresh leaves.

It is possible that the protein of the spinach leaves is in some form of combination with a substance of a pentosan nature, but confirmation of this has not yet been obtained. J. C. D.

Action of Hydrogen Cyanide on the Organism of Plants. Jules Stoklasa (*Compt. rend.*, 1920, **170**, 1404—1407).—Micro-organisms offer a considerable resistance to hydrogen cyanide. Exposure to an atmosphere containing 2% by volume of this gas for twenty-four hours at 13—14° only slackened the development without stopping it in the case of *B. subtilis* and *B. mesentericus vulgatus* and certain phycomycetes. *Tilletia tritici* was, however, completely destroyed by exposure to such a concentration for twenty-four hours at 16°. Such an exposure in no way injured the germination of wheat, barley, or beetroot seeds, provided the seeds were freely exposed to the air for three days and stirred frequently before germination. W. G.

Organic Chemistry.

Polymerisation. H. Staudinger (*Ber.*, 1920, **53**, [*B*], 1073—1085).—During recent years there has been a noticeable tendency to formulate polymerisation products as molecular compounds in which the individual portions are united by means of partial valencies. In the author's opinion, this tendency is to be deprecated, since, in the present state of our knowledge, such compounds can be represented by normal valency formulæ.

Polymerisation processes are defined as those in which two or more molecules unite to form a product of the same composition, but greater molecular weight. Two types of product are to be distinguished: (1) "true" polymerisation products, in which the atoms are united in the same manner as in the unimolecular compound (hexaphenylethane from triphenylmethyl, paraldehyde from acetaldehyde, etc.), and (2) "condensed" polymerisation products, in which a more or less atomic displacement has occurred (aldol polymerisation, benzoin formation, etc.). The first case only is discussed in the present communication. Polymerisation occurs with substances containing an unsaturated atom, or, more generally, with those which have an unsaturated linking, in which case rings containing 4, 6, or 8 atoms are formed, or else a product of very high molecular weight. It appears impossible at present to predict the direction in which action will take place. On the other hand, more general information is available on the stability of polymerides and their tendency towards depolymerisation. 4-Atom rings are generally less stable than those with 6 atoms, as is to be expected from Baeyer's strain theory. Heterocyclic four-membered rings are usually less stable than *cyclo*butane derivatives. The permanence of the latter, however, is greatly modified by substitution, and can be greatly weakened by the introduction of phenyl or carbonyl groups. The six-membered rings, particularly those which are *iso*cyclic, are relatively stable, though fission occurs more frequently with heterocyclic systems. The possibility of smooth depolymerisation to the unimolecular substance depends, not only on the temperature of decomposition of the polymeride, but also on the stability of the simpler compound.

In the light of these general considerations, the literature of the formation of four-, six-, and eight-membered rings is critically reviewed, and it is shown that all known stable polymerisation products can be expressed by formulæ with normal valencies. For the highly complex products, such as paraformaldehyde, the formula $\ldots \overset{H_2}{C}{\cdot}O{\cdot}\overset{H_2}{C}{\cdot} \ldots \overset{H_2}{C}{\cdot}O{\cdot}\overset{H_2}{C}{\cdot}O \ldots$ is proposed. Possible objection might be raised that free valencies are thus left at either end of the carbon chain; this would, however, only indicate the presence of two unsaturated positions in a highly complex molecule,

which would consequently be far less reactive than the simpler molecule. This accords well with the experimentally established fact that such polymerides are in general much less active than the simple substances, with which, however, they usually have certain actions in common. H. W.

Partial Condensation of Natural Gas at Liquid Air Temperatures and a Curious Effect Observed with the Nitrogen which Dissolves in the Condensate. JOHN SATTERLY (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 109—121).—Methods for the preliminary separation of natural gas by condensation are described. Sudden solution and expulsion of nitrogen by liquid methane occurred. [See *J. Soc. Chem. Ind.*, 1920, 539A.]

J. R. P.

The Oxidation of Paraffins. AD. GRÜN [with E. ULBRICH and TH. WIRTH] (*Ber.*, 1920, **53**, [*B*], 987—996).—The recent publication of Kelber (this vol., i, 280) has induced the author to place on record some of the results obtained by himself.

Under suitable conditions, pure paraffins, or mixtures such as vaselin or petroleum, are readily oxidised to fatty acids by air or even by gaseous mixtures containing as little as 1% of oxygen. The statements by various authors that the process can be catalytically accelerated by suitable oxygen carriers are, in general, erroneous, and depend, in part at any rate, on insufficiently extended analyses of the products. Thus a series of experiments carried out with a paraffin, m. p. 52°, at 160° showed that metallic oxides, such as lime and barium oxide, salts with an alkaline reaction, and certain neutral substances, such as carbon and fuller's earth, are particularly harmful, whilst acidic substances, such as stearic acid, are, according to the properties of the hydrocarbon used, either helpful or at any rate not markedly inhibitive. If the conditions of reaction are not carefully chosen, one carbon atom after another of the intermediate products can be oxidised away, and the whole series of acids from those of high molecular weight to the volatile acids, and ultimately to formic acid or carbon dioxide, may be obtained. Particularly when oxygen is used, the action is likely to lead to violent explosions, due to the intermediate formation of peroxides.

The products of oxidation differ not only quantitatively, but also qualitatively, according to the conditions of experiment. The most interesting observation is that, when the conditions are not too vigorous, the product consists of mixtures of waxes with more or less free acid, alcohols, and some unsaponifiable matter. The composition of the mixture of acids depends entirely on factors such as temperature, duration of action, etc., and may consist mainly of the series C_{16} to C_{22} or higher, or of such in which C_1 to C_{14} or C_{16} predominate. Hydroxy-fatty acids are also formed and are present partly in the form of esters or estolides, whilst unsaturated acids, probably derived from the hydroxy-acids by loss of water, are also found. The unsaponifiable matter consist

to a small extent of unchanged paraffin, but chiefly of higher alcohols with some carbonyl compounds. The separation of these products is a matter of difficulty, since the usual qualitative and quantitative carbonyl reactions are not trustworthy with substances of high molecular weight. Removal of the carbonyl derivatives is most readily effected indirectly by reducing them to alcohols by sodium and amyl alcohol, and their amount can be indirectly estimated by determining the hydroxyl number of the product before and after such treatment. They appear to consist of a mixture of aldehydes with certain amounts of ketones.

The results so far obtained do not permit any definite conclusion to be drawn with regard to the course of the oxidation; it would appear, however, that molecular oxygen attacks the carbon chain at a greater distance from the methyl group than is to be expected from analogous processes. H. W.

Fatty Acids Obtained by the Oxidation of Paraffins. FRANZ FISCHER and WILHELM SCHNEIDER (*Ber.*, 1920, **53**, [*B*], 922—925).—Pure paraffin or crude expressed paraffin is heated with dilute sodium carbonate solution in a steel autoclave at about 170°, whilst simultaneously compressed air is pumped through the mixture. The paraffins are considerably more rapidly oxidised under these conditions than at atmospheric pressure, and the yield of fatty acids is as high as 90% of the paraffin used. The rate of reaction depends on the temperature in the usual manner, and is proportional to the pressure of the air. Iron, manganese, and copper have approximately equal catalytic effects, but the other substances investigated are less active, possibly in part owing to the catalytic activity of the steel walls of the autoclave. Under the same conditions, the quantity of fatty acids produced per hour is, within limits, proportional to the amount of paraffin, but the highest yields per given time are best obtained by working so as to secure complete neutralisation of the sodium carbonate solution rather than complete utilisation of the paraffin. Examination of the fatty acids, which are purified in the usual manner, shows that they are true, monobasic fatty acids, the density of which is less than unity, and that they dissolve completely in light petroleum; unlike the more common members, however, they contain an uneven number of carbon atoms. The following have been definitely characterised: $C_{19}H_{38}O_2$, m. p. 65—66°; $C_{17}H_{34}O_2$, m. p. 58—59°; $C_{15}H_{30}O_2$, m. p. 50—51°; $C_{13}H_{26}O_2$, m. p. 38°.

Re-examination of a patented process for the oxidation of paraffin by blowing air through the substance heated at 135—145° in an iron vessel in the absence of water shows that the actual products are the acid anhydrides, which can be separated from unaltered paraffin by taking advantage of the insolubility of the latter in acetone. H. W.

The Constitution of the Mercury Compounds of Carbon Monoxide and of Ethylene. WILHELM MANCHOT (*Ber.*, 1920, **53**, [*B*], 984—987).—The author's experiments (the full details

of which will be published elsewhere) lead him to the conclusion that the ethylene compounds mentioned in the title are to be regarded as additive products of ethylene and basic mercury salt, $C_2H_4,Hg(OH)X$, and not as structural compounds, as formulated by Schoeller, Schrauth, and Essers (A., 1913, i, 1162; this vol., i, 225). The close similarity between these substances and those given by carbon monoxide indicates a similar structure for the latter also. This conclusion is supported by the fact that methyl acetatomercuriformate yields carbon monoxide, mercury iodide, and mercury acetate when heated with methyl iodide at 100°, whereas, according to the structural formulation, mercuric iodide and methyl acetate would be expected; similarly, ethyl chloromercuriformate and *n*-propyl iodide yield carbon monoxide and mercury haloid without a trace of methyl butyrate. Reaction appears to occur in accordance with the equation

$$CO,Hg(OEt)Cl + RI = CO + HgClI + R{\cdot}OEt.$$

The mercury derivatives obtained by Schoeller and Schrauth by the action of ethylene on an alcoholic solution of mercury acetate behave similarly to those prepared in aqueous solution and also to the carbon monoxide compounds; in particular, they are extremely readily decomposed by halogen acids, with liberation of ethylene, whilst the latter is also evolved when they are treated with alkyl iodides. Their constitution may therefore be expressed by the formula $C_2H_4,Hg(OEt)X$. H. W.

Preparation of Dimethylbutadiene. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 319505; from *Chem. Zentr.*, 1920, ii, 776).—Pinacone chlorohydrin is treated with hydroxyl-free substances which can combine with acids, such as ammonia or organic bases. Thus, when it is distilled with dimethylaniline, a mixture of water and dimethylbutadiene passes over between 60° and 80°. H. W.

Production of True Acetylenic Hydrocarbons from *epi*Dibromhydrin. R. LESPIEAU and BOURGUEL (*Compt. rend.*, 1920, **170**, 1584—1586).—*epi*Dibromohydrin, $CH_2Br{\cdot}CBr{:}CHBr$, reacts in the cold with mixed magnesium derivatives to give compounds of the type $CH_2{:}CBr{\cdot}CH_2R$, which, when acted on by alcoholic potassium hydroxide, lose the elements of hydrogen bromide, giving an acetylenic hydrocarbon, but the action is complicated by the tendency of the triple linking to migrate. A better method is to prepare a tribromide from the compound, $CH_2{:}CBr{\cdot}CH_2R$, and then act on this with sodium ethoxide, the product being $CHBr{:}CBr{\cdot}CH_2R$, which, when acted on by zinc in alcoholic solution, gives the required acetylenic hydrocarbon, $CH{:}C{\cdot}CH_2R$. Thus *epi*dibromohydrin condenses with magnesium ethyl bromide to give β-bromopentene, b. p. 107—108°, D_0^0 1·277. This compound unites with bromine to give *αββ-tribromopentane*, b. p. 108—109°/17 mm., D_0^0 2·03, which with sodium ethoxide yields *αβ*-dibromopentene, b. p. 66—67°/19 mm., D_0^0 1·73. This compound, whe

treated in alcoholic solution with zinc, gives Δ^a-pentinene, $CH{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$. W. G.

Production of Chloropicrin. KENNEDY JOSEPH PREVITÉ ORTON and (SIR) WILLIAM JACKSON POPE (Brit. Pat. 142878).—*Chloropicrin* is obtained by the action of chlorine in presence of water on picric acid or other suitable nitrophenol, a sufficient amount of alkali, preferably sodium hydroxide or carbonate, being added either before or during the reaction to dissolve the nitro-compound and neutralise the acid produced according to the equation $C_6H_2(NO_2)_3{\cdot}OH + 11Cl_2 + 5H_2O = 3CCl_3{\cdot}NO_2 + 13HCl + 3CO_2$. For example, 1 part of picric acid may be dissolved in a solution of 2·975 parts of sodium hydroxide in 50 parts of water, and, after cooling to 2—4°, whereby sodium picrate separates in small crystals, a slow, intermittent stream of chlorine is led in until the colour of the solution is discharged. The chloropicrin separates as an almost colourless oil, and amounts to 180—190% of the weight of picric acid taken. G. F. M.

The Effect of Reducing Agents on Tetranitromethane, and a Rapid Method of Estimation. AILEEN BAILLIE, ALEXANDER KILLEN MACBETH, and NORAH IRENE MAXWELL (T., 1920, **117**, 880—884).

Corrections for Densities of Ethyl Alcohol to 15·5°/15·5°. H. DROOP RICHMOND (*Analyst*, 1920, **45**, 222).—A table is given showing the *corrections* to be made when the *specific gravity* is determined at temperatures between 10° and 25°, and for a range in specific gravity from 0·79 to 0·99. W. P. S.

Preparation of Polyhydroxy-alcohols. OSCAR MATTER (D.R.-P. 299074; from *Chem. Zentr.*, 1920, iv, 14).—The requisite halogenated hydrocarbons are hydrolysed by aqueous solutions of carbonates or hydrogen carbonates, or mixtures thereof; as the reaction proceeds, the used hydrolysing agent is regenerated by addition of alkali hydroxide solution. Addition may be made periodically or continuously, at will or automatically. When using closed vessels, the concentration of the reagent may be maintained uniform during the whole experiment. The rate of reaction is thereby increased during the whole time, but particularly towards the end; concentrated products are obtained and the pressure in the vessel is lessened. The preparation of ethylene glycol from ethylene chloride and sodium carbonate or hydrogen carbonate at 130—140° is cited. H. W.

A Hydrate of an Oxonium Compound. O. MAASS and J. RUSSELL (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 259—264).—A termolecular compound of ethyl ether, hydrogen bromide, and water was isolated by the freezing-point curves of the system $(C_2H_5)_2O$,HBr and H_2O. The formula of the compound was found to be $(C_2H_5)_2O,HBr,H_2O$. The catalytic effect of mineral

acids in esterification is attributed to their linking the alcohol and organic acid in a molecular complex, where opportunity is afforded for interchange of radicles. A definite compound of ethyl alcohol and ethyl ether-hydrobromide could not be obtained. J. R. P.

Preparation of Ethylene Oxide. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 299682; from *Chem. Zentr.*, 1920, iv, 16).—(i) Bases are added to warm ethylene chlorohydrin or its solutions. (ii) When bases other than alkalis are used, the order of addition of the substances may be changed. Excellent yields of ethylene oxide are obtained, whereas ethylene glycol and polyethylene glycols are mainly produced when the chlorohydrin is added to the warm alkali solution. H. W.

The Xanthates of Cobalt and Nickel. MARCEL DELÉPINE and LOUIS COMPIN (*Bull. Soc. chim.*, 1920, [iv], **27**, 469—474. Compare this vol., i, 536, and Dubsky, A., 1914, ii, 732).—These xanthates were prepared by double decomposition with alkali xanthates. The nickel salts crystallise much more readily than the cobaltic salts, the former being also more stable than the latter. As with the dithiocarbamates, there is a tendency to get some cobaltous salt along with the cobaltic salt, the tendency increasing with the molecular weight. The nickel salts are black, the cobaltic salts deep green or black, and the cobaltous salts brown. The salts described are *cobaltic methylxanthate*; cobaltic and nickel ethylxanthates (compare Dubsky, *loc. cit.*); *cobaltic* and *nickel n-propylxanthates*, *cobaltic* and *nickel* n-*butylxanthates* and iso*butylxanthates*; *cobaltic*, *cobaltous*, and *nickel* iso*amylxanthates*; *cobaltic* and *cobaltous benzylxanthates*; *cobaltic* iso*propylxanthate*; *cobaltic* and *nickel* sec.-*butylxanthates*; *cobaltic* and *cobaltous menthylxanthates*. W. G.

Trimethylsulphonium Compounds. HILDEGARD BLÄTTLER (*Monatsh.*, 1919, **40**, 417—429).—The author has prepared a number of double compounds formed from trimethylsulphine chloride, bromide, and iodide with a number of metallic salts. Methods are given for the preparation of methyl hydrogen sulphate and methyl sulphide.

Unlike methyl iodide, methyl chloride combines with difficulty with methyl sulphide, this combination not being aided materially by addition of zinc chloride or cadmium chloride, although the formation of double sulphinium compounds from metallic salt, sulphide, and alkyl haloid often proceeds considerably more readily than the union of sulphide and alkyl haloid alone. For the preparation of the other double chlorides, use was made, therefore, of trimethylsulphine chloride previously obtained.

Trimethylsulphine chloride is best obtained by treating an aqueous solution of the corresponding iodide with silver chloride; it decomposes at 100°, and has m. p. 100—117°.

Bistrimethylsulphine cupric chloride, $(SMe_3)_2CuCl_4$, forms orange-yellow crystals, which soften and turn black at 180° and melt com-

pletely at 190°. *Bistrimethylsulphine zinc chloride*, $(SMe_3)_2ZnCl_4$, white, non-hygroscopic crystals, m. p. 208°. *Trimethylsulphine cadmium chloride*, SMe_3CdCl_3, white, non-hygroscopic needles or fan-like aggregates, subliming slightly, but not melting, at 430°. *Bistrimethylsulphine manganous chloride*, $(SMe_3)_2MnCl_4$, pale yellow, non-hygroscopic crystals, remaining unchanged at 300°. *Trimethylsulphine ferrous chloride*, SMe_3FeCl_3, m. p. (impure?) 190°. *Trimethylsulphine ferric chloride*, SMe_3FeCl_4, pale yellowish-brown crystals, softening at 240°, m. p. 250°. *Trimethylsulphine bismuth chloride* (?), SMe_3BiCl_4 (?), white, crystalline precipitate. *Trimethylsulphine stannic chloride*, SMe_3SnCl_5, white precipitate, unmelted at 300°.

Trimethylsulphine bromide (compare Cahours, this Journ., 1875, 1181; 1876, i, 696; Carrara, A., 1892, 1422), readily obtained from the iodide and silver bromide, forms colourless, transparent, deliquescent plates, and begins to melt at 184° and volatilises completely at 189°. With copper bromide in methyl-alcoholic solution, it gives a deep violet precipitate, m. p. 184—185°. *Bistrimethylsulphine zinc bromide*, $(SMe_3)_2ZnBr_4$, forms white, non-hygroscopic crystals, m. p. 211—213°. *Trimethylsulphine cadmium bromide*, SMe_3CdBr_3, white, non-hygroscopic crystals, sinters at about 180°, m. p. (frothing) 233—235°. *Bistrimethylsulphine bismuth bromide*, $(SMe_3)_2BiBr_5$, pale yellow precipitate, swells at about 220°, m. p. 223°.

Trimethylsulphine iodide has m. p. 184—185° (compare Klinger, A., 1878, 128; Strömholm, A., 1900, i, 325). *Bistrimethylsulphine zinc iodide*, $(SMe_3)_2ZnI_4$, forms white, non-hygroscopic crystals, m. p. 183°. *Trimethylsulphine bismuth iodide*, SMe_3BiI_4, red salt, not melting at 290° (compare Vanino and Mussgnug, A., 1917, i, 196). T. H. P.

Preparation of ββ′-Dichloroethyl Sulphide. (SIR) WILLIAM JACKSON POPE, CHARLES STANLEY GIBSON, and HENRY FLEETWOOD THUILLIER (Brit. Pat. 142875).—ββ′-Dichloroethyl sulphide is obtained in upwards of 90% yield by passing dry ethylene into sulphur monochloride heated to, and maintained at, 50—70°, until no further absorption occurs. The reaction is facilitated by introducing a small proportion of dichloroethyl sulphide into the sulphur monochloride before treatment with ethylene. The product is conveniently separated from the sulphur simultaneously formed by heating the reaction mixture to 100° and allowing to cool, when the sulphur is deposited in crystalline form and the supernatant liquid can be poured off. G. F. M.

ββ′-Dichlorodiethyl Sulphide and certain of its Derivatives. WILHELM STEINKOPF, JULIUS HEROLD and JOSEPH STOHR (*Ber.*, 1920, **53**, [*B*], 1007—1012).—ββ′-Dichlorodiethyl sulphide, $S(CH_2\cdot CH_2Cl)_2$, is readily prepared as a colourless oil, b. p. 108—109°/15 mm. (yield, 83%), by the action of thionyl chloride on ββ′-dihydroxydiethyl sulphide in the presence of chloroform. It is oxidised by hydrogen peroxide to the corresponding

sulphoxide, m. p. 109°, and by potassium permanganate to the *sulphone*, colourless crystals, m. p. 48°, b. p. 179—181°/14—15 mm. β-Hydroxydiethyl sulphide, $SEt\cdot CH_2\cdot CH_2\cdot OH$, b. p. 182—184°, is conveniently obtained by the addition of ethylene chlorohydrin to ethyl mercaptan dissolved in a solution of sodium in alcohol. It is converted by phosphorus tribromide into *β-bromodiethyl sulphide*, b. p. 83—86°/29 mm. *ββ'-Dibromodiethyl sulphide*, from ββ'-dihydroxydiethyl sulphide and phosphorus tribromide, has b. p. 115·5°/1 mm., m. p. 31—34°. *ββ'-Dithiocyanodiethyl sulphide* is prepared by heating the corresponding chloride with sodium thiocyanate in acetone solution; it forms bright yellow crystals, m. p. 35°. ββ'-Dicyanodiethyl sulphide could not be prepared, but *ββ'-dicyanodimethyl sulphide*, m. p. 47·5°, b. p. 177—178°/22 mm., was obtained by the action of potassium sulphide on chloroacetonitrile. *Phenyl β-chloroethyl sulphide*, $CH_2Cl\cdot CH_2\cdot SPh$, b. p. 144·5°/26 mm., 245°/atmospheric pressure, was prepared from ethylene chlorohydrin and thiophenol in the presence of a solution of sodium in ethyl alcohol. H. W.

Reactions and Derivatives of ββ'-Dichlorodiethyl Sulphide. OREGON B. HELFRICH and E. EMMET REID (*J. Amer. Chem. Soc.*, 1920, **42**, 1208—1232).—*ββ'-Dichlorodiethyl sulphoxide*,

$$(CH_2Cl\cdot CH_2)_2SO,$$

plates, m. p. 109·5°, is obtained by diluting a solution prepared by the addition of ββ'-dichlorodiethyl sulphide to concentrated nitric acid at the ordinary temperature. On distillation, even under reduced pressure, it is partly decomposed into the sulphide, but it is unchanged by boiling water or silver nitrate solution; alcoholic sodium hydroxide converts it into *dihydroxydiethyl sulphoxide*, $(HO\cdot CH_2\cdot CH_2)_2SO$, a viscous, oily liquid, easily soluble in water. The dichloro-compound apparently has no action on the skin, whereas *dichlorodiethylsulphone*, $(CH_2Cl\cdot CH_2)_2SO_2$, leaflets, m. p. 56°, b. p. 183°/20 mm., causes blisters and persistent sores, and also has a lachrymatory, and a slight sternutatory, effect. The physiological activity of these compounds appears to be parallel to the extent to which they suffer hydrolysis (compare Marshall, *J. Amer. Med. Assoc.*, 1919, **73**, 684), for the sulphone reacts partly with boiling aqueous silver nitrate solution. It is obtained from the sulphoxide by oxidation with fuming nitric acid, potassium permanganate, or, most satisfactorily, a solution containing 5—10% of chromic acid and 15—18% of sulphuric acid. The sulphone suffers decomposition at 230° when distilled under atmospheric pressure. *ββ'-Dihydroxydiethylsulphone*,

$$(HO\cdot CH_2\cdot CH_2)_2SO_2,$$

is a viscous, somewhat deliquescent syrup, b. p. 140—165°/15 mm. Condensation products of the sulphide, sulphoxide, and sulphone with sodium salts of phenols, thiophenols, alcohols, mercaptans, and with aromatic amines have been prepared. *Di-β-phenylthioldiethyl sulphide*, $(SPh\cdot CH_2\cdot CH_2)_2S$, m. p. 57·5°. *Di-β-phenylthioldiethyl sulphoxide*, $(SPh\cdot CH_2\cdot CH_2)_2SO$, m. p. 121·0°. *Di-β-*

henylthioldiethylsulphone, $(SPh\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 104·5°. *i-β-phenylsulphinyldiethyl sulphoxide*, $(SOPh\cdot CH_2\cdot CH_2)_2SO$, a. p. 161°. *Di-β-phenylsulphinyldiethylsulphone*, $(SOPh\cdot CH_2\cdot CH_2)_2SO_2$, a. p. 164°. *Di-β-phenylsulphonyldiethylsulphone*, $(SO_2Ph\cdot CH_2\cdot CH_2)_2SO_2$, ı. p. 235°. *Di-β-phenoxydiethyl sulphide*, $(OPh\cdot CH_2\cdot CH_2)_2S$, ı. p. 54·2°. Di-β-phenoxydiethylsulphone, $(OPh\cdot CH_2\cdot CH_2)_2SO_2$, ı. p. 108°. *Di-β-p-tolyloxydiethyl sulphide*, $(C_6H_4Me\cdot O\cdot CH_2\cdot CH_2)_2S$, a. p. 78°. *Di-β-p-tolyloxydiethylsulphone*, $(C_6H_4Me\cdot O\cdot CH_2\cdot CH_2)_2SO_2$, a. p. 120°. *Di-β-o-tolyloxydiethyl sulphide*, m. p. 46·5°. *Di-β-α-aphthoxydiethyl sulphide*, $(C_{10}H_7\cdot O\cdot CH_2\cdot CH_2)_2S$, m. p. 94·5°. *i-β-β-naphthoxydiethyl sulphide*, m. p. 129°. *Di-β-β-naphthoxy-iethylsulphone*, $(C_{10}H_7\cdot O\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 151°. *Di-β-anilloxydiethyl sulphide*, $[OMe\cdot C_6H_3(CHO)\cdot O\cdot CH_2\cdot CH_2]_2S$, m. p. 131·5°. *Di-β-eugenoxydiethyl sulphide*, $[CH_2{:}CH\cdot CH_2\cdot C_6H_3(OMe)\cdot CH_2\cdot CH_2]_2S$, m. p. 113·5°. *Di-β-2:4:6-tribromophenoxydiethyl sulphide*, $(C_6H_2Br_3O\cdot CH_2\cdot CH_2)_2S$, m. p. 118·5°. *Di-β-butylthioldiethyl sulphide*, $(C_4H_9\cdot S\cdot CH_2\cdot CH_2)_2S$, m. p. 17·5°, b. p. 222—223°. *Di-β-butylthioldiethyl sulphoxide*, $(C_4H_9\cdot S\cdot CH_2\cdot CH_2)_2SO$, m. p. 25°. *Di-β-butylthioldiethylsulphone*, $(C_4H_9\cdot S\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 73·7°. *Di-β-butylsulphinyldiethyl sulphoxide*, $(C_4H_9\cdot SO\cdot CH_2\cdot CH_2)_2SO$, m. p. 196°. *Di-β-butylsulphinyldiethylsulphone*, $(C_4H_9\cdot SO\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 101°. *Di-β-butylsulphonyldiethylsulphone*, $(C_4H_9\cdot SO_2\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 266·5°. *Di-β-ethylthioldiethyl sulphide*, $(SEt\cdot CH_2\cdot CH_2)_2S$, m. p. 17°, b. p. 173—175°. *Di-β-ethylthioldiethylsulphone*, $(SEt\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 64°. *Di-β-ethylsulphonyldiethylsulphone*, $(SO_2Et\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 223°. *Di-β-methylthioldiethylsulphone*, $(SMe\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 77°. *Di-β-propylthioldiethyl sulphide*, $(SPr\cdot CH_2\cdot CH_2)_2S$, m. p. 27·5°, b. p. 193—195°. *Di-β-propylthioldiethylsulphone*, $(SPr\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 75·5°. *Di-β-propylsulphonyldiethylsulphone*, $(SO_2Pr\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 254°. *Di-β-isobutylthioldiethylsulphone*, $(C_4H_9\cdot S\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 94·2°. *Di-β-sec.-butylthioldiethylsulphone*, $(C_4H_9\cdot S\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 15°. *Di-β-amylthioldiethyl sulphide*, $(C_5H_{11}\cdot S\cdot CH_2\cdot CH_2)_2S$, m. p. 20°. *Di-β-amylthioldiethylsulphone*, $(C_5H_{11}\cdot S\cdot CH_2\cdot CH_2)_2SO_2$, m. p. 91°. 4-*Phenyl*-1:4-*thiazan*, $NPh{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}S$, m. p. 108—111°. 4-*Phenyl*-1:4-*thiazan* 4-*oxide*, $NPh{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}SO$, m. p. 123·5°. 4-p-*Tolyl*-1:4-*sulphonazan*, $C_6H_4Me\cdot N{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}SO_2$,

m. p. 136·5°. 4-o-*Tolyl*-1 : 4-*sulphonazan*, m. p. 135°. *Di-β-acetoxydiethyl sulphide*, $(OAc\cdot CH_2\cdot CH_2)_2S$, b. p. 155—156°/20 mm., D^{20} 1·132, $n^{22\cdot 5}$ 1·4720. Of the compounds, $(R\cdot O\cdot CH_2\cdot CH_2)_2S$, only those could be obtained in which R = aromatic radicle.

ββ'-Di-iododiethyl sulphide, $(CH_2I\cdot CH_2)_2S$, m. p. 55—60°, the *sulphoxide*, $(CH_2I\cdot CH_2)_2SO$, m. p. 104·5°, and the sulphone, $(CH_2I\cdot CH_2)_2SO_2$, m. p. 203°, were obtained from the chloro-derivatives and sodium iodide.

A report on the physiological activity of the above compounds, which is in general slight, is included in the paper. J. K.

Ethylene Sulphide, C_2H_4S. MARCEL DELÉPINE (*Compt. rend.*, 1920, **171**, 36—38).—Chloroethyl thiocyanate is decomposed by an aqueous solution of sodium sulphide, giving sodium thiocyanate, sodium chloride, and *ethylene sulphide*, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!>\!S$, a colourless liquid, b. p. 55—56°, D_4^0 1·0368—1·0342, n_D^{18} 1·4914—1·49001. The material slowly polymerises spontaneously, and very rapidly in the presence of some reagents, to give a white solid. With methyl iodide, it gives a crystalline *compound* having all the characteristics of a sulphinium iodide. This iodide with silver chloride gives a crystalline *chloride*, yielding a *platinichloride*. W. G.

Organic Derivatives of Tellurium. II. Constitution of the Dimethyltelluronium Dihaloids. RICHARD HENRY VERNON (T., 1920, **117**, 889—898).

Production of Acetic Acid from Paracetaldehyde as the Primary Material. SOCIÉTÉ DES ACIERIES & FORGES DE FIRMINY (Brit. Pat. 124195).—Paracetaldehyde is directly converted into acetic acid by electrolytic oxidation, using a porous cathode, for example, gas carbon, and a refractory anode, such as magnetite or platinum. The electrolyte consists of 10% sulphuric acid, in which the paracetaldehyde dissolves to the extent of 10—15%. Any excess is allowed to float on the surface, and dissolves as the oxidation proceeds. Oxidation is facilitated by the addition to the bath of a small quantity of a salt of a metal capable of plurality of degrees of oxidation, such as manganese, cerium, molybdenum, or vanadium. A high current density is employed and the acetic acid is allowed to accumulate to a concentration of about 40%, when it is separated from the sulphuric acid by distillation. G. F. M.

Manufacture of Ethyl Acetate from Paracetaldehyde as the Primary Material. SOCIÉTÉ DES ACIERIES & FORGES DE FIRMINY (Brit. Pat. 131600).—By adding to the mixture of acetic acid and dilute sulphuric acid produced by the electrolytic oxidation of paracetaldehyde (preceding abstract) a quantity of ethyl alcohol equivalent to the acetic acid which it contains, and distilling the whole on a rectifying apparatus, esterification is effected and pure ethyl acetate distils. The liquid remaining containing

sulphuric acid and a little non-esterified acid and alcohol may be again employed as a basis for a fresh electrolysis. G. F. M.

Poly-iodide Compounds of Oxalic Esters. ANTON SKRABAL and ELEONORE FLACH (*Monatsh.*, 1919, **40**, 431—444).—The authors have prepared a number of compounds analogous to the double compound of potassium periodide and ethyl oxalate (compare Skrabal, A., 1917, i, 378) and differing essentially only in degree of stability. These compounds mostly crystallise well and always exhibit a dark colour and metallic lustre, which is frequently combined with pleochroism. They exhibit the characters of the poly-iodides, including the tendency to decompose with liberation of iodine; the pressure at which such decomposition occurs furnishes a measure of the stability.

Study of the dissociation equilibria of these compounds shows that the tendency of the iodides of the alkali metals to form compounds with iodine and ethyl oxalate increases in passing from sodium to potassium and then diminishes in passing to rubidium and cæsium, ammonium occupying a position near that of potassium; the sodium compound does not correspond in composition with the others. Further, a poly-iodide compound with a bromide as component is of far lower stability than that with the corresponding iodide as component.

The compounds, which have all been prepared either in aqueous solution or in presence of water, apparently belong to the oxonium compounds, but it is undecided whether it is the carbonyl or the ethereal oxygen atom of the oxalic ester which assumes the oxonium valencies. The following compounds are described:

Compounds of ethyl oxalate: Sodium periodide compound,

$$(C_6H_{10}O_4)_4,NaI,I_4,$$

small, reddish-brown crystals. Potassium periodide,

$$(C_6H_{10}O_4)_2,KI,I_2,$$

small, brown to violet, highly stable crystals (*loc. cit.*). *Rubidium periodide*, $(C_6H_{10}O_4)_2,RbI,I_2$, dark brown crystals with metallic lustre. *Ammonium periodide*, $(C_6H_{10}O_4)_2,NH_4I,I_2$, bluish-black crystals with metallic lustre, highly stable. *Caesium periodide*, $(C_6H_{10}O_4)_2,CsI,I_2$, shining, dark brown crystals. *Potassium perbromide*, $(C_6H_{10}O_4)_2,KBr,I_2$, unstable, shining, golden-brown scales. *Sodium mercuric periodide*, $(C_6H_{10}O_4)_4,3NaI,HgI_2,I_4$, reddish-brown crystals, readily emitting iodine. *Potassium mercuric periodide*, $(C_6H_{10}O_4)_8,4KI,HgI_2,I_8$, reddish-brown crystals. *Potassium cadmium periodide*, $(C_6H_{10}O_4)_{10},6KI,CdI_2,I_{10}$, shining, brownish-green crystals, readily losing iodine. *Potassium bismuth periodide*, $(C_6H_{10}O_4)_6,3KI,BiI_3,I_6$, reddish-brown powder. In all these compounds, one molecule of ethyl oxalate corresponds with one atom of periodine.

Compounds of methyl oxalate: Potassium periodide,

$$(C_4H_6O_4)_2,KI,I_4,$$

shining, bluish-black crystals. *Rubidium periodide*,

$$(C_4H_6O_4)_2,RbI,I$$

lark crystals. In these compounds, one molecule of the methyl ester :orresponds with two atoms of periodine.

Compounds of methyl ethyl oxalate: Potassium periodide,

$$(C_5H_8O_4)_2,KI,I_2,$$

orown crystals. *Rubidium periodide*, $(C_5H_8O_4)_2,RbI,I_2$, dark orown crystals. *Ammonium periodide*, $(C_5H_8O_4)_2,NH_4I,I_2$, dark olue crystals.

Compounds of tetraethyl semi-ortho-oxalate: Potassium periodide, $(C_{10}H_{20}O_5)_2,KI,I_2$, brownish-violet, stable crystals.

Compounds of tetramethyl semi-ortho-oxalate: Potassium periodide, $(C_6H_{12}O_5)_3,2KI,I_4$, dark blue to black crystals, and

$$(C_6H_{12}O_5)_2,KI,I_4,$$

brownish-black powder, readily emitting iodine. T. H. P.

Periodides of Carbonyl Compounds. A. M. CLOVER (*J. Amer. Chem. Soc.*, 1920, **42**, 1248—1260. Compare A., 1904, i, 322).—Reviewing the isolated instances in the literature of periodides derived from organic compounds free from nitrogen, the author concludes that it is the carbonyl group which is essentially involved in their structure, and suggests the designation " carbonyl periodides," including among them the periodides of dimethyl- and tetramethyl-pyrones, and of amides, and anilides. Coumarin potassium periodide (Dox and Gaessler, A., 1917, i, 346. Compare Morgan and Micklethwait, T., 1906, **89**, 866) is best purified by the addition of ether to its concentrated solution in alcohol or ethyl acetate, and has the formula $(C_9H_6O_2)_3,2KI,I_5,H_2O$. *Methyl oxalate potassium periodide*, $(C_4H_6O_4)_2,KI,I_6$, separates from a mixture of aqueous solutions of its components as fine crystals with a dark bluish-grey lustre, m. p. 55—75°. Benzamide potassium periodide (Moore and Thomas, A., 1914, i, 1130), after crystallisation from ether, melts at 130°, and has the formula

$$(C_7H_7ON)_3,2KI,I_5.$$

Succinimide potassium periodide, $(C_4H_5O_2N)_4,KI,I_2$, m. p. 141—149°, separates as light brown, lustreless crystals from an alcoholic solution of its components. Succinic anhydride potassium periodide, $(C_4H_4O_3)_4,KI,I_2$, previously described (*loc. cit.*), separates as crystals with a green lustre from a mixture of ethyl acetate and chloroform. From barbituric acid, two *compounds* result, according to the proportions of the components mixed in aqueous solution; in one case, yellow crystals, $(C_4H_4O_3N_2)_7,2KI,I_6$, in the other, green crystals, $(C_4H_4O_3N_2)_2,2KI,I_5$, are obtained. *Diethylbarbituric acid potassium periodide*, $(C_8H_{12}O_3N_2)_2,KI,I_4$, from aqueous solutions of its components, forms crystals with a steel-blue lustre, m. p. above 200°. In other cases, there is evidence of formation of compounds, although they cannot be isolated. Thus many organic ketones, anhydrides, esters, etc., dissolve iodine and potassium iodide to a considerable extent, although the solubility of each of these is limited. In this manner, acetone furnishes dark green, needle-shaped crystals of a potassium iodide periodide, and needles with a golden lustre of a sodium iodide periodide. Also, often as a result of fusion or grinding together of the com-

ponents, a strong metallic lustre is developed, and iodine is not so readily lost by volatilisation from the product; in other cases, a lustrous residue is left on evaporation of a solution of the components. J. K.

The Tartaric Acid Compounds of Antimony. A. Blanchetière (*Bull. Soc. chim.*, 1920, [iv], **27**, 477—490).—The velocity of solution of freshly-prepared antimony hydroxide in a solution of tartaric acid agrees with Jungfleisch's theory of esterification and not with the formation of a salt. This action, relatively rapid at first, diminishes in velocity very quickly when the ratio of tartaric acid to antimony hydroxide dissolved is about two, but the solution will proceed until this ratio becomes one, after a very long time. Using *d*-tartaric acid, these solutions, when evaporated, give syrupy solutions, which only crystallise with difficulty. If racemic acid is used, the material can be separated, by evaporation, into monoantimonyltartaric acid and ill-defined products. The best method of preparation of this acid is to extract the complexes, richer in tartaric acid, with acetone. Precipitation methods only give a hydrophile gel of the required acid containing a varying excess of tartaric acid. W. G.

Compounds and Derivatives of *d*-Glucose-6-bromohydrin. Emil Fischer, Burckhardt Helferich, and Paal Ostmann (*Ber.*, 1920, **53**, [*B*], 873—886).—It is shown that many of the reactions of acetylbromoglucose can be extended to acetyldibromoglucose and that, under suitable conditions, compounds are formed which retain the terminal bromine atom in the place of the hydroxyl group of the sugar molecule. The configuration of all these compounds is the same as that of *d*-glucose.

β-Methyl-d-*glucoside-ζ-bromohydrin*,

$$OMe\cdot\underbrace{CH\cdot[CH(OH)]_2\cdot CH}_{O}\cdot CH(OH)\cdot CH_2Br,$$

prisms, m. p. about 148° (decomp.), $[\alpha]_D^{15}$ −35·12° in aqueous solution, is obtained by the action of a methyl-alcoholic solution of ammonia on triacetylmethylglucoside-6-bromohydrin. It is hydrolysed by *N*-hydrochloric acid with the formation of ζ-bromoglucose, which, however, could only be obtained as a syrup, but could be identified by conversion into d-*glucose-ethylmercaptal-ζ-bromohydrin*, long, silky needles, m. p. 107° (corr. decomp.), $[\alpha]_D^{10}$ +4·92° in alcoholic solution.

Tetra-acetyl-d-*glucose-ζ-bromohydrin*, needles or four-sided prisms, m. p. 127° (corr.) after previous softening, is prepared by treating a hot solution of acetyldibromoglucose in glacial acetic acid with dry silver acetate.

Acetyldibromoglucose is converted, when boiled with water, into a mixture of ζ-bromoglucose (identified as the ethylmercaptal) and anhydroglucose (compare Fischer and Zach, A., 1912, i, 239, 678), which was isolated from the product in the form of its p-*bromophenylhydrazone*, pearly leaflets, m. p. 184° (corr.) after slight previous softening, to a reddish-brown syrup; the substance

exhibits mutarotation when dissolved in dry pyridine, $[\alpha]_D^{18}$ having the initial and final values $-18{\cdot}89°$ and $-10{\cdot}86°$ respectively. It is decomposed by formaldehyde, yielding anhydroglucose, m. p. 118° (corr.), $[\alpha]_D + 51{\cdot}4°$, whereas Fischer and Zach give $+53{\cdot}7°$.

Triacetyl-β-theophylline-d-*glucoside-ζ-bromohydrin*,

$$C_7H_7O_2N_4\cdot CH\cdot[CH(OAc)]_2\cdot CH\cdot CH(OAc)\cdot CH_2Br,$$

is prepared from acetyldibromoglucose and the silver derivative of theophylline in boiling xylene solution and forms slender needles, m. p. 193—194° (corr.), $[\alpha]_D^{15} -9{\cdot}92°$ in tetrachloroethane solution. It is hydrolysed by methyl-alcoholic ammonia to *β-theophylline*-d-*glucoside-ζ-bromohydrin*, coarse prisms, $+2{\cdot}5H_2O$; the anhydrous substance has m. p. about 217° (decomp.) after slight softening, $[\alpha]_D^{18} -18{\cdot}99°$ in aqueous solution, $[\alpha]_D^{18} -13{\cdot}87°$ in *N*-hydrochloric acid solution, mutarotation not being observed in either instance. The triacetyl compound is reduced by zinc dust and acetic acid to *triacetyl-β-theophylline*-d-iso*rhamnoside*, m. p. 230° (corr.), after slight previous softening, which does not exhibit appreciable optical activity when dissolved in tetrachloroethane or glacial acetic acid; *it is transformed by a solution of ammonia in methyl alcohol into* *β-theophylline*-d-iso*rhamnoside*,

$$C_7H_7O_2N_4\cdot CH\cdot[CH(OH)]_2\cdot CH\cdot CHMe\cdot OH,$$

m. p. 254° (corr.), $[\alpha]_D^{16} -22{\cdot}27°$ in aqueous solution.

Triacetylthiocyanoglucose-ζ-bromohydrin,

$$CSN\cdot CH\cdot[CH(OAc)]_2\cdot CH\cdot CH(OAc)\cdot CH_2Br,$$

slender, interwoven needles, m. p. 164-5° (corr.) after previous softening, $[\alpha]_D^{18} +16{\cdot}14°$ in tetrachloroethane solution, is prepared from acetyldibromoglucose and silver thiocyanate, and is converted by boiling alcohol into *triacetyl*-d-*glucosethiourethane-ζ-bromohydrin*, $OEt\cdot CS\cdot NH\cdot CH\cdot[CH(OAc)]_2\cdot CH\cdot CH(OAc)\cdot CH_2Br$, thin silky leaflets, m. p. 128—129° (corr.), $[\alpha]_D^{15} +10{\cdot}27°$ in tetrachloroethane solution.

H. W.

Biochemical Preparation of Sucrose from Gentianose. Em. Bourquelot and M. Bridel (*Compt. rend.*, 1920, **171**, 11—15).—By the action of emulsin, freed as completely as possible from invertase, on a solution of gentianose, a mixture of dextrose and sucrose was obtained. The dextrose was converted into β-methylglucoside and the sucrose isolated in a pure crystalline state.

W. G.

The Action of Radium Radiation on Sucrose and Agar. A. Fernau (*Biochem. Zeitsch.*, 1920, **102**, 246—251).—Sucrose is inverted by the action of radium radiation. Agar submitted to the same influence liquefies with the production of sugars (most probably galactose and arabinose) which reduce strongly Fehling's solution. The chemical change in both cases is due to the primary action of the radium.

S. S. Z.

Alteration of Volume in the Inversion of Sucrose. N. SCHOORL (*Zeitsch. Nahr. Genussm.*, 1920, **39**, 113—121).—A discussion on the contraction in volume occurring when sucrose is hydrolysed by acid. The contraction for one gram-molecule of sucrose and one gram-molecule of water is 6·9 c.c., which corresponds approximately with 0·5 c.c. for 26 grams of sucrose per 100 c.c. of water. W. P. S.

The Hydrolysis of the Polysaccharides. E. HILDT (*Compt. rend.*, 1920, **170**, 1505—1507. Compare A., 1919, ii, 84).—A further examination of the use of the mixture of sulphuric acid and sodium benzenesulphonate in the molecular proportions of 1 : 2 for the hydrolysis of disaccharides. It is shown that both dextrose and galactose are unaltered by this reagent, retaining their rotatory and reducing powers. Non-lævulosic sugars, such as lactose, maltose, or glycogen, are not hydrolysed at the ordinary temperature by this catalyst, but in the case of sugars, such as sucrose, raffinose, or inulin, the lævulose is completely split off after the lapse of a considerable time at the ordinary temperature, or in less than one hour at 95—98° in the case of sucrose and raffinose. W. G.

Iron Salt of Carbohydrate-Phosphoric Acid. KARL SCHWEIZER (*Mitt. Lebensmit. Hyg.*, **11**, 16—23; from *Chem. Zentr.*, 1920, i, 881).—*Iron zymophosphate*, $C_6H_{10}O_4(PO_4Fe)_2$, is a greyish-green, tasteless, and odourless powder, which decomposes without melting at 200°. For its preparation, a solution of sucrose (100 grams) in distilled water (250 c.c.) is treated with commercial expressed yeast (150 grams) and toluene (1 c.c.); after ten minutes, a solution of disodium phosphate (80 grams) in water (300 c.c.) is added, and, after four hours, the yeast is removed, preferably by centrifuging. The liquid is heated to 60°, and, after removal of precipitated albumin, is treated with a saturated solution of ferrous chloride (14 grams). The separation of the precipitate is facilitated by the addition of an equal volume of alcohol (90%) to the solution; it is purified by repeated grinding with water. The salt is decomposed by hydrochloric, nitric, sulphuric, and acetic acids, the iron passing thereby into the ionised state; with sodium hydroxide, a precipitate of iron hydroxide is formed. The salt is decomposed in the stomach, both iron and phosphoric acid being converted into forms which are readily absorbed. H. W.

Hydrogen Peroxide as Solvent. MAX BAMBERGER and JOSEF NUSSBAUM (*Monatsh.*, 1919, **40**, 411—416).—Concentrated aqueous hydrogen peroxide solutions, and in higher degree the almost anhydrous peroxide obtained from these by freezing, serve as excellent solvents for many organic compounds. Among the latter are compounds rich in hydroxyl groups, and the higher the molecular weight of these compounds, the more concentrated must be the peroxide solution necessary to effect solution.

For instance, 60% aqueous hydrogen peroxide solution dissolves

starch, giving solutions which are viscous or dough-like, according to the concentration. Cellulose and its decomposition products are also soluble, and the less the extent to which the cellulose has been altered, the greater the concentration of the peroxide required for solution. From these solutions, precipitants, such as water, throw out the cellulose in chemically modified form, and the solutions themselves undergo gradually increasing change in properties. Cellulose wool, as used for preparing cellulose nitrate, dissolves to the extent of 25%, the tenacious dough thus formed becoming more and more mobile when kept out of contact with atmospheric moisture. The products precipitated from these solutions differ from those obtained by the action of sulphuric acid on cellulose, no substance coloured blue by iodine being formed.

With peroxide solution weaker than that necessary for solution, cellulose swells, and cotton wool thus treated shows under the microscope swollen fibres with a greatly diminished lumen; flattened or damaged portions of the fibres dissolve the more readily, the double refraction and the visibility of the fibres disappearing as dissolution proceeds.

In spite of its negative heat of formation, anhydrous hydrogen peroxide is not explosive, and a large quantity of it cannot be exploded by means of a 2-gram mercury fulminate cap. In conjunction with certain organic compounds, however, the peroxide yields powerful explosives capable of technical application.

Sugars and proteins also dissolve in concentrated hydrogen peroxide solutions. The latter produce no apparent change in pure, white wool, but when this is withdrawn and well washed with water, the fibres exhibit considerable strength, and are almost as elastic as rubber; after being dried, these fibres completely lose their elasticity.

The action of the peroxide on substances dissolved in it seems to be of the nature of a decomposition or depolymerisation. Thus paraformaldehyde yields formaldehyde, or, under some conditions formaldehyde peroxide (compare Legler, A., 1883, 860; 1886, 327 Nef, A., 1898, i, 111).

In working with concentrated hydrogen peroxide solutions, great cleanliness is necessary, since contamination with catalysts, for instance, iron, manganese, or lead, causes very vigorous decompositions, which are accompanied by generation of heat, and may produce ignition. Such mixtures burn in the air with hissing, like smokeless powder. Ignition may be produced by sprinkling powdered lead peroxide or iron pyrites on the peroxide solution.

T. H. P.

Constitution of Cellulose. I. Acetolysis of Ethyl Cellulose KURT HESS and WALTER WITTELSBACH (*Zeitsch. Elektrochem.* 1920, **26**, 232—251).—The various formulæ proposed for cellulose are discussed. The formation of ω-bromo-5-methylfurfuraldehyde from cellulose and from dextrose (Fenton and Gostling, T., 1901 **79**, 361, 807) suggests that, contrary to the formulæ of Green (T., 1906, **89**, 811), cellulose contains dextrose residues in the same

form as dextrose itself. The production of lævoglucosan from starch as readily as from cellulose, to which it bears no resemblance (Pictet and Sarasin, A., 1918, i, 58), discounts the idea of any constitutional similarity between lævoglucosan and cellulose, but suggests that it owes its origin to dextrose residues present in each. In confirmation of the view that the hydrofuran ring of lævoglucosan is not present in cellulose, it is shown that ethyl cellulose, on distillation under reduced pressure, gives no ethyl lævoglucosan, but only a small proportion of an oily product. As a basis for a new formula for cellulose, it is pointed out that all five hydroxyl groups of dextrose are etherifiable, as evidenced by the tannins (E. Fischer, A., 1913, i, 1352; 1919, i, 278) and certain bisaccharides (Haworth and Leitch, T., 1918, **113**, 188; 1919, **115**, 809; Irvine and Dick, T., 1919, **115**, 593). Formulæ, too complicated to be reproduced, are therefore discussed in which the hydroxyl groups of a dextrose or cellobiose molecule are etherified by molecules of dextrose or cellobiose. In order to reach some decision between the numerous possibilities of such an arrangement, the work of Ost (A., 1906, i, 560) and of Madsen (*Diss.*, Hanover, 1917) on the production of cellobiose acetate and dextrose penta-acetate is reviewed, in conjunction with a repetition of their experiments. The conclusion is that the probable maximum yield of each from ten parts of air-dry cellulose is 6·2 grams of cellobiose acetate and 12 grams of dextrose penta-acetate. It has not been possible to attain the higher yields recorded by Ost in certain experiments. The dextrins, which occur in the form of acetates when the maximum proportion of cellobiose acetate is not reached, are looked on as mixed partial degradation products of the cellulose molecule, resulting from the removal by hydrolysis in a variety of ways of one or more dextrose or cellobiose residues. The formula $OX\cdot\underbrace{CH\cdot[CH(OX)]_2\cdot CH}_{O}\cdot CH(OX)\cdot CH_2\cdot OX$, in which X represents the residue, $\underbrace{CH\cdot[CH(OH)]_2\cdot CH}_{O}\cdot CH(OH)\cdot CH_2\cdot OH$, requires that 9·38 grams of cellulose should give 6·42 grams of cellobiose acetate and 12·51 grams of dextrose penta-acetate, whilst the other alternatives require widely different quantities. Although the arbitrary nature of this formula, in view of the evidence available, is recognised, it is adopted as a working basis. In accordance with it, Denham and Woodhouse (T., 1913, **103**, 1735; 1914, **105**, 2357) considered dextrose to be among the products of hydrolysis of methyl cellulose. Evidence of a similar nature is presented from the results of hydrolysis of an ethyl cellulose, containing 2·5 ethyl groups per dextrose residue (or 3 per residue with free hydroxyl groups in the formula), under conditions of acetolysis much milder than those usual in the case of cellulose, and such that hydrolysis of ethoxy-groups, as might occur with hydrochloric acid, did not occur. It follows from the formula that the ethoxy-numbers of the ethyl dextrins produced in the form of acetates as intermediate products of acetolysis will always be less than that of the original ethyl cellulose, and, a point not explained by previous

formulæ, when degradation has proceeded sufficiently far, less than that of the ethyl glucoses, which, in the form of acetates, will also have a lower ethoxy-number than ethyl cellulose. Repeated experiments uniformly confirmed this, and the ethoxy-number of the sugar portion at the outset (36·5) was much higher than that for diethyl triacetylglucose (21·6%), the formation of which the older formulæ would suggest. The marked difference between cellulose and its derivatives, for example, nitrate, acetate, and the products obtained by the action of acids, alkalis, or zinc or copper ammonium compounds, is accounted for by considering such derivatives to be derived from the above simple formula, which is taken as representing hydrocellulose (for which the name celluxose is now proposed), whilst cellulose is a condensation product of a number of such molecules. The results of Stern (T., 1904, **85**, 336), Stein (*Diss.*, Dresden, 1911), and Ost (A., 1913, i, 833) show that little, if any, elimination of water can be assumed in this condensation, and it is suggested that the separate molecules are united through residual affinities of hydroxyl groups. The ability of alcohols of all kinds (Grün and others, A., 1908, i, 934; 1910, i, 352; Vanino and Hartl, A., 1906, i, 785), of dextrose (Lippmann, *Chemie der Zuckerarten*, I, 549), and of its esters and glucosides (Fischer and Hess, A., 1912, i, 415) to form double compounds with metallic salts is in accord with this idea, which leads to a simple explanation of the disintegrating effect of zinc chloride, ammonia, and similar reagents on cellulose as due to their competition for the residual valencies responsible for the complexity of the cellulose molecule. Ethyl cellulose is a derivative of celluxose, since its acetolysis takes place under much less stringent conditions than that of cellulose, and the heat of reaction is slight; the contrast in this respect with cellulose is only partly accounted for by the greater number of hydroxyl groups in cellulose, and is chiefly due to the difference in distribution of valency in the two cases. It is also suggested that the physical characteristic of cellulose as a hollow thread is reproduced in the arrangement of the celluxose molecules in the cellulose complex, and that this complex may be partly broken down by mechanical means, for example, in the case of "totgemahlener" cellulose, which represents a stage of disintegration approaching the less profound of those produced chemically. Similar considerations may apply to the molecules of hemicelluloses, protein, and caoutchouc, but the case of starch is left open. J. K.

Cellulose and its Esters. I. Fractional Precipitation of Cellulose Nitrates. J. Duclaux and (Mme) E. Wollman (*Bull. Soc. chim.*, 1920, [iv], **27**, 414—420).—By fractional precipitation of cellulose nitrate from its solution in acetone by aqueous acetone or water, it is possible to divide it into a number of fractions which have widely different viscosities in 2% acetone solution. By repeating this process with the extreme fractions, fractions were ultimately obtained the viscosities of which in acetone solution were as 46 : 1, and at one end a cellulose nitrate was obtained which in

1% *acetone solution* was as viscous as glycerol. These various fractions have not undergone any change in the fractionation, since they obey the law of mixtures in so far as their viscosities are concerned. Further, the nitrogen content of the different fractions of one and the same operation is sensibly the same. A better method of separation of the fractions rather than by fractional precipitation is probably by the use of a series of ultra-filters. The different cellulose nitrates can best be characterised and differentiated by osmotic pressure measurements. W. G.

The Viscosity of Solutions of Nitrocellulose in Mixtures of Acetone and Water. IRVINE MASSON and ROBERT McCALL (T., 1920, **117**, 819—823).

The Viscosity of Solutions of Cellulose Nitrate in Ether-Alcohol. WILLIAM HOWIESON GIBSON and ROBERT McCALL (*J. Soc. Chem. Ind.*, 1920, **39**, 172—176T).—With a given cellulose nitrate, the viscosity of its solution in an ether–alcohol mixture is dependent on the ratio of ether to alcohol, and reaches a minimum value at a definite ratio. This optimum ratio is independent of the concentration of the cellulose nitrate, but is affected by the nitrogen content.

The optimum composition of an ether–alcohol solvent for a cellulose nitrate is not affected by the addition of glyceryl nitrate. Glyceryl nitrate, when added to solutions of cellulose nitrate in ether–alcohol, tends to increase the viscosity of the solution. W. G.

Measurement of the Viscosity of Pyroxylin Solutions. E. F. HIGGINS and E. C. PITMAN (*J. Ind. Eng. Chem.*, 1920, **12**, 587—591).—Efflux viscosimeters are only suitable for pyroxylin solutions of low viscosity, and the steel ball viscosimeter (T., 1920, **117**, 473) for those of very high viscosity. The most generally applicable instrument is Stormer's viscosimeter, in which the viscosity is calculated from the speed of rotation of a cylinder in the liquid. When absolute viscosities are plotted as ordinates against the times of 100 revolutions as abscissæ, the points will be found to lie along a straight line. The equation is therefore of the type $V=At+B$, where B is the value of V when $t=0$. In the case of the particular instrument used, when $t=0$, $V=-25=B$. By substituting this value for B at any point of the curve, the value for $A=4{\cdot}6$. The equation for calculating absolute viscosity from the observed readings when a 150-gram counterweight was used was therefore $V=4{\cdot}6t-25$. The speed of revolution varies directly with the magnitude of the counterweight. The correction for the friction factor is practically a constant over a viscosity range of 20 to 500 centipoises. C. A. M.

The Neutral Hydrolysis of Guncotton. The Alkaline Hydrolysis of Guncotton. E. KNECHT and B. R. BOSTOCK (*J. Soc. Chem. Ind.*, 1920, **39**, 163—165T).—When guncotton is heated with water in a sealed tube at 190°, it undergoes hydrolysis, the

guncotton disappearing and a pale straw-coloured liquid being left. The rate of hydrolysis depends on the relative proportions of guncotton and water used. If the temperature is lowered by more than about 2°, the hydrolysis is extremely slow, and if it is raised 10—15°, a considerable amount of charring takes place. The amount of gas given off by heating 0·5 gram of guncotton with 25 c.c. of water for half-an-hour at 190° is 99 c.c. The gas consists of carbon monoxide and dioxide and nitrous oxide and nitrogen. Some hydrocyanic acid and ammonia are found in the solution. Of the 13·05% of nitrogen originally present in the guncotton, 10·24% is found as nitrous oxide and nitrogen, 0·43% as hydrogen cyanide, 1.20% as ammonia, 0·12% as nitrate, and 0·27% undetermined.

When guncotton is dissolved in aqueous sodium hydroxide on a water-bath, it is found that 65% of the total nitrate nitrogen is reduced to nitrite in order to provide the oxygen for the organic oxidation products which result from the hydrolysis. The extent of this reduction is nothing like so great in the alkaline hydrolysis as in the neutral aqueous hydrolysis. W. G.

Non-existence of Valence and Electronic Isomerism in Hydroxylammonium Derivatives. ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1920, **42**, 1232—1245).—A theoretical paper in which the alkyl hydroxylammonium salts are discussed with regard to their formation and constitution. The author comes to the conclusion that since isomeric trialkyl-hydroxylammonium salts and trialkyl-dialkyloxyammonium derivatives are unknown, there is no experimental evidence in this field to support Werner's ammonium or co-ordination hypotheses, or any modification of them. Neither are any facts known which substantiate electronic conceptions, or the existence of "electromers" in this group o compounds. J. F. S.

Salts of *N*-Methylhexamethylenetetramine. R. TSCHUNK. (U.S. Pat. 1336709).—Salts of *N*-methylhexamethylenetetramin are produced by treating a mixture of formaldehyde and ammoni with methylating agents (such as methyl sulphate, methyl thic cyanate, methyl nitrate, methylamine thiocyanate, or chlorobromc methane) in the presence of acid anions, heating for some time and allowing the product to crystallise. The thiocyanate, meta borate, dichromate, ferrocyanide, picrate, perchlorate, chlorate nitrate, sulphate, acetate, and salicylate are mentioned, and detail of the methods of making them are given.

CHEMICAL ABSTRACTS.

The Metallic Dithiocarbamates, especially those of Cobal and Nickel. LOUIS COMPIN (*Bull. Soc. chim.*, 1920, [iv], **27** 464—469. Compare Delépine, *ibid.*, 1908, [iv], **3**, 643).—Th author has prepared certain dithiocarbamates of cobalt, nickel, an copper by double decomposition of salts of these metals with th sodium dithiocarbamates. The cobaltic salt obtained is alway accompanied by a certain amount of cobaltous salt, and in one o two cases it was possible to isolate the latter salts. The followin

salts were prepared: *Sodium, cobaltic,* and *nickel methyldithiocarbamates; sodium* and *cobaltic ethyldithiocarbamates; sodium, cobaltic,* and *nickel propyldithiocarbamates.* These sodium and nickel salts were all crystalline, but the cobaltic salts were only obtained with difficulty. *Copper dimethyldithiocarbamate; cobaltic, nickel,* and *copper diethyldithiocarbamates; potassium cobaltic, nickel,* and *copper dipropyldithiocarbamates; cobaltic diallyldithiocarbamate: cobaltic di*-iso*butyldithiocarbamate; cobaltic, cobaltous, nickel,* and *copper di*-iso*amyldithiocarbamates; potassium, cobaltic,* and *cobaltous dibenzyldithiocarbamates; sodium* and *cobaltic methylphenyldithiocarbamates; sodium* and *cobaltic piperidyldithiocarbamates;* and *cobaltic tetrahydro*iso*quinolyldithiocarbamate.* W. G.

Is the Direct Synthesis of Carbamide by Urease Possible? TH. J. F. MATTAAR (*Rec. trav. chim.*, 1920, **39**, 495—498).—The author has repeated Barendrecht's work (this vol., i, 195) on the action of the urease in soja flour on ammonium carbonate, and has also used a sample of urease prepared by the method of van Slyke and Cullen (A., 1914, ii, 822), and finds no evidence that the synthesis of carbamide takes place; but, on the contrary, finds that any carbamide introduced into such a solution of ammonium carbonate containing the urease is destroyed. W. G.

Arsine Thiocyanates and certain other Organic Derivatives of Arsenic. WILHELM STEINKOPF and WALTER MIEG (*Ber.*, 1920, **53**, [*B*], 1013—1017).—Attempts have been made to prepare arsine thiocyanates of the general form, $RAs(SCN)_2$ and $R_2As{\cdot}SCN$, by the action of solutions of sodium thiocyanate in acetone on the corresponding chlorides. Under these conditions, methylarsine dichloride gave only products which were extremely readily decomposed by moisture with the production of amorphous, yellow substances, and which could not be distilled even under diminished pressure, whilst arylarsine dichlorides could not be caused to react in the desired sense. On the other hand, products of the type $R_2As{\cdot}SCN$, in which R is an alkyl or aryl radicle, could be obtained in several cases as fairly stable substances. Improved methods of preparing some arsine chlorides are given and certain new members of this series are described.

Ethyldichloroarsine, b. p. 145—150°, is conveniently prepared from arsenic trichloride and mercury diethyl, and is converted by potassium hydroxide in the presence of benzene and a little water into ethylarsine oxide, AsEt:O, colourless oil, b. p. 158°/10 mm., which readily becomes oxidised on exposure to air. iso*Amyldichloroarsine*, from *iso*amylarsinic acid and phosphorus trichloride in chloroform solution, is a colourless liquid, b. p. 88·5—91·5°/15 mm., which is decomposed by water. α-Naphthyldichloroarsine has m. p. 68°. Cacodyl chloride is obtained by the action of sodium hypophosphite on cacodylic acid in the presence of concentrated hydrochloric acid, and has b. p. 106·5—107°; it does not fume on

exposure to the atmosphere, and is rapidly converted by dry air into a crystalline oxidation product. *Cacodyl thiocyanate*, $AsMe_2 \cdot SCN$, b. p. 92°/17 mm., is a colourless oil which gradually becomes yellow when preserved. *Phenyldimethylarsine dichloride*, $AsMe_2PhCl_2$, m. p. 134° (decomp.), is prepared by the addition of chlorine to phenyldimethylarsine and is decomposed at 180°, yielding *phenylmethylchloroarsine*, b. p. 229—232°. *Diphenylarsine thiocyanate* has b. p. 230—233°/22—23 mm.; it is decomposed by water with the elimination of the thiocyano-group.
H. W.

Chemical Actions of Penetrating Radium Radiation. XI. Influence of Penetrating Rays and of Ultra-violet Light on Toluene alone and in Presence of Water. ANTON KAILAN (*Monatsh.*, 1919, **40**, 445—466. Compare A., 1918, i, 209).—Exposure of toluene in the dark for about two years to the action of the radiation from a preparation containing 0·080 gram of radium in a glass envelope 1 mm. in thickness, results in attack of less than 0·25% of the toluene, the products formed including benzaldehyde, benzoic acid, and apparently formic acid. The increase in the density of the toluene and the weight of the residue left on evaporation indicate that the principal product of the reaction consists, not of benzoic acid, but of a yellow viscous mass composed presumably of hydrocarbons and of condensation products of benzaldehyde (compare Ciamician and Silber, A., 1912, i, 174). Changes of similar nature and order of magnitude are produced in toluene, exposed for twenty-two hours to the radiation from a quartz mercury lamp at a distance of 8—9 cm.

The action of radium radiation on toluene in presence of water yields three times as much acid as in absence of water, benzoic and formic acids being produced, together with a non-acid residue. As regards the action on toluene of the radiation from a quartz mercury lamp, this is not increased by the presence of water to the same extent as the action of radium radiation, but oxalic acid is then produced, as well as benzoic and formic acids. T. H. P.

The Catalysing Action of Aluminium in the Preparation of Chlorobenzenes. JEAN MEUNIER (*Compt. rend.*, 1920, **170**, 1451—1452).—In the preparation of chlorobenzene, one part of aluminium to one thousand of benzene acts as a very satisfactory catalyst, the absorption of chlorine proceeding smoothly. The action should be stopped when the density of the liquid reaches 1·008. W. G.

The Replacement of Substituents in the Benzene Nucleus. A. F. HOLLEMAN and A. J. DEN HOLLANDER (*Rec. trav. chim.*, 1920, **39**, 435—480. Compare A., 1916, i, 22; 1918, i, 216).—The eleven dichlorodinitrobenzenes have been prepared and their behaviour in the presence of sodium methoxide studied. Three of these compounds are new.

By hydrolysis of 3:6-dichloro-2-nitroacetanilide, and subsequent

replacement of the amino-group by a nitro-group by the method of Körner and Contardi (compare A., 1914, i, 263), 1:4-*dichloro-2:3-dinitrobenzene*, m. p. 103°, is obtained, which is identical with Jungfleisch's β-dichlorodinitrobenzene obtained in the preparation of 1:4-dichloro-2:6-dinitrobenzene (compare *Ann. Chim. Phys.*, 1868, [iv], **15**, 259).

1:4-*Dichloro-2:5-dinitrobenzene*, m. p. 119°, is prepared by the hydrolysis of 3:6-dichloro-4-nitroacetanilide, and replacement of the amino-group by a nitro-group. Alternatively, this compound may be prepared by nitrating 4-chloro-3-nitroacetanilide, hydrolysing the product, diazotising the amine, and introducing a chlorine atom by the Gattermann reaction. The authors consider that the compounds described under the name 1:4-dichloro-2:5-dinitrobenzene by Morgan and Norman (T., 1902, **81**, 1378, 1382), Hartley and Cohen (T., 1904, **85**, 868), and Nason (A., 1919, i, 10) are either impure or different isomerides.

By the chlorination of 2:5-dinitroaniline by hydrochloric acid and potassium chlorate, a mixture of two compounds, which were not isolated, was obtained. This mixture was diazotised, and the resulting diazonium salts submitted to the Gattermann reaction. By this means, 1:4-dichloro-2:5-dinitrobenzene mixed with a small amount of 1:2-*dichloro-3:6-dinitrobenzene*, m. p. 60°, was obtained. Several attempts to prepare the last-named compound by other methods were unsuccessful.

From a qualitative and quantitative study of the action of sodium methoxide on the chloronitrobenzenes, it is shown that the activity of a replaceable chlorine atom is increased considerably by the introduction of a nitro-group into the para- or ortho-positions, and that the activity of a nitro-group becomes greater on the introduction of a chlorine atom, more particularly in the meta-position. The introduction of a second nitro-group into the chloronitro- and dichloronitro-benzenes renders the chlorine atoms in the meta-position to the nitro-group already present inactive. On the other hand, when the two nitro-groups are in a meta-position to one another, it is always a chlorine atom which is attacked. W. G.

Nitration of *m*-Nitrotoluene. M. D. MARQUEYROL, M. G. A. KOEHLER, and JOVINET (*Bull. Soc. chim.*, 1920, [iv], **27**, 420—424).—By the nitration of *m*-nitrotoluene with a mixture of 16 parts of sulphuric acid (96%) and 2·25 parts of nitric acid (88%) for eight hours at 100°, a mixture of three trinitrotoluenes, namely, 2:3:4-, 3:4:6-, and 2:3:6- or 2:3:5-trinitrotoluenes, is obtained.

W. G.

Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. II. The Dinitrotoluenes. JAMES KENNER and MICHAEL PARKIN (T., 1920, **117**, 852—859).

2:3:6-Trinitrotoluene: a New Synthesis. OSCAR LISLE BRADY and ARTHUR TAYLOR (T., 1920, **117**, 876—880).

Trinitration of *o*-Xylene. M. D. MARQUEYROL and P. LORIETTE (*Bull. Soc. chim.*, 1920, [iv], **27**, 424—426).—By passage through its mono- and dinitro-derivatives without purification of these, but using fresh nitration mixtures at each stage, the two trinitro-*o*-xylenes, previously described by Crossley and Renouf (compare T., 1909, **95**, 202), were obtained from *o*-xylene. W. G.

Preparation of Condensation Products from *N*-Arylsulpho-derivatives of Aromatic Aminosulphonic Acids. SOCIETY OF CHEMICAL INDUSTRY IN BASEL (D.R.-P. 319713; from *Chem. Zentr.*, 1920, ii, 777).—Formaldehyde is caused to react with *N*-arylsulphonyl derivatives of aminosulphonic acids of the benzene or naphthalene series. Examples are given of the condensation of *p*-toluenesulphonylsulphanilic acid in sodium carbonate solution, of *p*-toluenesulphonyl-1-aminonaphthalene-6-sulphonic acid in dilute sodium carbonate solution, and of amino-*p*-toluenesulphonyl-1-aminonaphthalene-6-sulphonic acid in acetic acid solution with formaldehyde. The products are soluble in water, precipitate albumin, and tan hide. H. W.

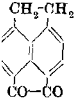
The Constitution of Anthracene. K. VON AUWERS (*Ber.*, 1920, **53**, [*B*], 941—944).—During recent years, a variety of chemical evidence in favour of the orthoquinonoid structure of anthracene has been adduced, and this is now supplemented by physical evidence. If this mode of formulation be correct, the system would contain a continuous chain of four conjugated double bonds which could not neutralise one another, and although this system is twice broken, and by reason of its position in the rings would probably not exhibit its full activity, it should, nevertheless, show strong exaltation of the refractive and the dispersive power. On the other hand, a compound with a para-linking in the central ring should show, at most, little exaltation, since the benzene nuclei are so disposed that active conjugations are not existent, and the para-bond is known in analogous cases to have little, if any, effect. Anthracene itself is unsuitable for investigation on account of its high melting point, but 9-*iso*amylanthracene has been investigated and found to exhibit very marked optical exaltation, which is very much less in evidence in the case of its dihydro-derivative, which behaves precisely as if it contained two benzene nuclei.

The following constants are recorded: 9-*iso*Amylanthracene, m. p. 58°, (i) $D_4^{76\cdot5}$ 0·9982, $n_\alpha^{76\cdot5}$ 1·62353, $n_D^{71\cdot6}$ 1·63475, $n_\beta^{76\cdot5}$ 1·67008, (ii) $D_4^{74\cdot}$ 0·9987, $n_\alpha^{71\cdot1}$ 1·62491, $n_D^{71\cdot1}$ 1·63636, $n_\beta^{71\cdot1}$ 1·67152. Dihydro-9-*iso*amyl-anthracene, (i) b. p. 202°/23 mm., $D_4^{45\cdot1}$ 1·0022, D_4^{20} 1·025, $n_\alpha^{45\cdot1}$ 1·56091 $n_D^{45\cdot1}$ 1·56584, $n_\beta^{45\cdot1}$ 1·58047, n_D^{20} 1·5771, (ii) b. p. 201—205°/17 mm. $D_4^{44\cdot4}$ 0·9940, D_4^{20} 1·016, $n_\alpha^{44\cdot4}$ 1·55791, $n_D^{44\cdot4}$ 1·56261, $n_\beta^{44\cdot4}$ 1·57651 n_D^{20} 1·5736. H. W.

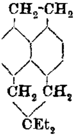
Derivatives of Acenaphthene. KARL FLEISCHER and PAUL WOLFF (*Ber.*, 1920, **53**, [*B*], 925—931).—The recent publication of Mayer and Kaufmann (this vol., i, 301) on a similar topic has

caused the authors to communicate the results obtained by themselves in this field.

A *diacetylacenaphthene*, colourless needles, m. p. 146°, has been isolated from the less volatile products obtained in the preparation of 5-acetylacenaphthene. The latter readily condenses with benzaldehydes to yield well-crystallised benzylidene derivatives, of which the *o-chlorobenzylidene* compound forms yellow prisms, m. p. 113°. 5-Acetylacenaphthene is reduced to 5-ethylacenaphthene, colourless, mobile oil, b. p. 158°/13 mm., m. p. 42·5—43°, D 1·0407, *n* 1·6117, by amalgamated zinc and hydrochloric acid (compare Mayer and Kaufmann, *loc. cit.*). The latter condenses with acetyl chloride in the presence of aluminium chloride to yield 6(?)-*acetyl-5-ethylacenaphthene*, m. p. 110·5°, which gives nicely crystalline benzylidene derivatives with aromatic aldehydes, and is reduced by Clemmensen's method to 5:6(?)-diethylacenaphthene, pale yellow oil, b. p. 182°/14 mm., m. p. 10—11°.



The author's attempts to introduce a second ethylene bridge in the *peri*-position in the acenaphthene molecule date back to 1911; for this purpose, oxalyl chloride does not appear to be a suitable reagent, but better results can be obtained with oxalyl bromide, which yields the substance (annexed formula), yellow crystals, m. p. 226° after slight previous softening and darkening. (The authors propose to call the substance *pyracenehemiquinone* and the parent ydrocarbon *pyracene*.)



Bromoacetyl bromide condenses with acenaphthene in the presence of aluminium chloride to yield 5-*bromoacetylacenaphthene*, pale grey, crystalline powder, m. p. 180°, and a *substance*, small, yellow needles, m. p. 94—96°, which could not be definitely identified.

A hydrocarbon closely allied to the hypothetical pyracene has been isolated by the reduction, by phosphorus and hydriodic acid, of 2:2-diethyl*peri*acenaphthindan-1:3-dione (Freund and Fleischer, A., 1910, i, 490; 1913, i, 1073), which yields :2-*diethyl*peri*acenaphthindane* (annexed formula), centimetre-ong crystals, m. p. 93—95°. H. W.

New Synthesis of Perylene. FRITZ HANSGIRG and ALOIS ZINKE *Monatsh.*, 1919, **40**, 403—404).—Perylene may be obtained in ood yield by heating 2:2′-dihydroxy-1:1′-dinaphthyl to a high emperature (400—500°) with a halogen compound of phosphorus PCl_5, PCl_3, $POCl_3$, PBr_5), addition of phosphorous acid being of dvantage. Hydrogen phosphide and small proportions of free hosphorus are formed during the reaction. T. H. P.

New Derivatives of Perylene. ALOIS ZINKE and ERNA INTERKREUTER (*Monatsh.*, 1919, **40**, 405—410).—*Perylene hexa-*

hydride, $C_{20}H_{18}$, prepared by heating perylene with hydriodic acid and red phosphorus at 200—210°, forms almost colourless, rhombohedral plates, m. p. 183—184° (uncorr.), which gradually turn yellow, especially in the light. It appears to sublime unchanged when very cautiously heated, but yields perylene when distilled over heated asbestos. It dissolves in warm concentrated sulphuric acid, giving a red solution.

Trinitroperylene, $C_{20}H_9(NO_2)_3$, prepared by the action of nitric acid (D 1·10) at 100°, crystallises in needles, decomposes at about 365°, and yields a violet-red solution in warm, concentrated sulphuric acid.

Tetranitroperylene, $C_{20}H_8(NO_2)_4$, prepared by boiling perylene with concentrated nitric acid (D 1·4), forms deep brick-red leaflets and darkens at above 300°. With warm sulphuric acid, it gives a red solution.

The oxidation of perylene to perylenequinone is effected readily by boiling the hydrocarbon with aqueous chromic acid solution.

Perylenequinol dibenzoate, $C_{20}H_{10}O_2Bz_2$, prepared from perylenequinone by Scholl and Mansfeld's method (A., 1910, i, 494), forms bundles of yellow needles, m. p. 295—296° (uncorr.), and yields a reddish-yellow solution with concentrated sulphuric acid.

Dibromoperylenequinone, $C_{20}H_8O_2Br_2$, crystallises in needles or leaflets, decomposes at about 412°, and dissolves in concentrated sulphuric acid to a violet-red solution.

Nitroperylenequinone, $C_{20}H_9O_2{\cdot}NO_2$, forms brownish-red needles and exhibits no sharp melting point. It colours cotton violet and gives a violet-red solution in concentrated sulphuric acid. Its *bromo*-derivative, $C_{20}H_8O_2Br{\cdot}NO_2$, forms red needles and dyes cotton brown. T. H. P.

The Determination of the Relative Strengths of some Nitrogen Bases of the Aromatic Series and of some Alkaloids. FRANCIS ARNALL (T., 1920, **117**, 835—839).

Preparation of Methyl Derivatives of Arylamino-compounds. ALPHONSE MAILHE (Brit. Pat. 124219).—Mono- and di-methylated arylamines are obtained by passing a mixture of the vapours of the arylamine and methyl alcohol over a suitable catalyst, preferably precipitated alumina, at a temperature of 350—400°, condensing the product, and separating the methylated bases from the condensate. The catalyst is conveniently spread on trays or plates arranged in a series of tubes built into a suitable furnace. The mixture of mono- and di-methylarylamines produced by this process may, if desired, be converted entirely into the di-methylated amine by passing the vapour mixed with a further quantity of methyl alcohol a second time over the catalyst. The exhausted catalyst can be regenerated by calcination in air. Examples are given of the preparation of the mono- and di-methyl-anilines, -toluidines, -xylidines, and -naphthylamines. G. F. M.

The Sulphonation of *m*-Sulphanilic Acid. S. C. J. Olivier (*Rec. trav. chim.*, 1920, **39**, 499—504).—The author confirms Schultz's view (A., 1906, i, 837) as to the composition of the disulphonic acid obtained by the sulphonation of 3-aminobenzene-1-sulphonic acid by Limpricht and Drebes (*Ber.*, 1876, **9**, 552). When the aminobenzenedisulphonic acid is diazotised in hydrochloric acid solution and then treated with copper, on neutralising the solution with potassium hydroxide, *potassium 2-chlorobenzene-1 : 4-disulphonate* is obtained, which yields *2-chlorobenzene-1 : 4-disulphonyl chloride*, m. p. 96·5—97°. This acid chloride, when heated in a sealed tube with phosphorus pentachloride for four hours at 210°, gives 1 : 2 : 4-trichlorobenzene, m. p. 17—18°.

W. G.

Vanillylamine. E. K. Nelson (U.S. Pat. 1329272).—An alcoholic solution of vanillin is treated with hydroxylamine hydrochloride and sodium carbonate, the excess of alcohol is evaporated after keeping in a warm place for twenty-four hours, and vanillin-oxime is precipitated by water. The oxime in alcoholic solution is reduced by 2·5% sodium amalgam with the gradual addition of glacial acetic acid to maintain an acid reaction. Vanillylamine is then isolated as the hydrochloride. Chemical Abstracts.

Some Observations on the "Springing" of "Carbolate" and the Recovery of Phenol from the Resulting Aqueous Layer. H. M. Dawson (*J. Soc. Chem. Ind.*, 1920, **39**, 151—152T).—The loss of phenol in the aqueous layer when a solution of sodium phenoxide is neutralised by sulphuric acid is minimised by keeping the volume of the aqueous layer as small as possible, and thereby increasing the salting-out effect of the sodium sulphate. The percentage loss can be calculated from the formula

$$p=75\cdot5\ (10^{1\cdot92-0\cdot0036C_2})/C_2,$$

where C_2 is the concentration of sodium sulphate (anhydrous) in grams per litre. Experiments were made to recover the phenol from the aqueous layer by extracting with different organic solvents. When 50 grams of the solvent were shaken at 25° with a litre of a solution containing 10 grams of phenol and 200 grams of sodium sulphate, *o*-cresol and *m*-cresol each extracted 75% of the phenol, nitrobenzene 65%, benzene 41%, solvent naphtha (b. p. 145—155°) 10%, and light petroleum (b. p. 95—100°) 4·7%. E. H. R.

Esterification with Phenols. M. Bakunin and F. Giordani (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1916, [iii], **22**, 125—134).—The interaction of a phenol and an anhydride serves as a general method for preparing esters in good yields. Various esters have been prepared in this way and their melting points determined by means of Pomilio's apparatus, in which electrical heating is employed.

With quinol and acetic anhydride, the product obtained forms white, micaceous scales, m. p. 119·4°, the reaction being greatly facilitated by the presence of a small proportion of phosphoric oxide, fuming sulphuric acid, or ferric or zinc chloride. These

condensing agents appear to exert, not a dehydrating action, but a catalytic effect, probably of ionic character (compare Bakunin, A., 1916, ii, 421).

The acetyl derivatives of the three nitrophenols are obtained by boiling together the phenol (1 mol.) and acetic anhydride (1 mol.) for ten to fifteen minutes, the presence of fused sodium acetate (compare Noelting, Grandmougin, and Michel, A., 1893, i, 90) being unnecessary. Acetyl-*p*-nitrophenol has m. p. 78·2°, and m-*nitrophenyl acetate*, $NO_2\cdot C_6H_4\cdot OAc$, crystallises in straw-yellow, shining needles, m. p. 53·5°.

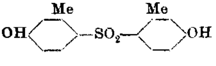
The acetyl derivatives of the three hydroxybenzoic acids may be prepared similarly (compare Oddo and Manuelli, A., 1897, i, 180), the melting points being 137°, 124·1°, and 180·5° for the ortho-, meta-, and para-compounds respectively. Here also phosphoric oxide, fuming sulphuric acid, and zinc chloride act as catalysts, but the actions are not so energetic as with the dihydroxybenzenes and require initial heating.

Phenylcinnamic anhydride, $(C_{15}H_{11}O)_2O$, obtained by boiling the acid with phosphoric oxide in chloroform solution (compare Bakunin, *loc. cit.*), forms crystals, m. p. 120·5°, and gives rather low values for the molecular weight in freezing benzene, owing possibly to the presence of a little unchanged acid or to dissociation of the anhydride. The phenylcinnamyl derivatives of the three dihydroxybenzenes, $C_6H_4O_2(C_{15}H_{11}O)_2$, have the melting points 154·2°, 162·4°, and 230° for the ortho-, meta-, and para-compounds (compare Bakunin, *loc. cit.*) respectively. T. H. P.

Preparation of Derivatives of *N*-Acylated *p*-Aminophenols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 318803, additional to D.R.-P. 316902; from *Chem. Zentr.*, 1920, iv, 15).—*N*-Acyl derivatives of the urethanes of *p*-aminophenols are treated with α-bromodiethylacetyl haloids. The preparation of the bromodiethylacetylurethane of *p*-acetylaminophenol from p-*acetylaminophenylurethane*, m. p. 181°, is described. The latter is obtained from guaiacolurethane and *p*-acetylaminophenol by distillation of the guaiacol at 150° or by reduction of p-*nitrophenylurethane*, m. p. 161°, by hydrogen in the presence of colloidal palladium. p-*Aminophenylurethane hydrochloride* has m. p. about 235° after softening above 200°, and is acetylated by a mixture of sodium acetate, acetic acid, and acetic anhydride. H. W.

***m*-Hydroxytolylsulphones.** JOSEF ZEHENTER (*Monatsh.*, 1919, **40**, 377—389).—The action of sulphuric acid (about 30% SO_3) on *m*-cresol at 140° yields the following two *m*-hydroxytolylsulphones, the β-compound being formed in small proportion.

α-m-*Hydroxytolylsulphone* (annexed constitution) crystallises in plates or prisms ($+\frac{1}{2}H_2O$), m. p. 115—116°, and dissolves readily in alkali hydroxides or ammonia, giving solutions from which it is precipitated by addition of acid.



s *tetrabromo*-derivative, $C_{14}H_{10}O_4Br_4S$, forms almost colourless. icular crystals, m. p. 225°. Its *diacetyl* compound,

$$C_{14}H_{12}O_4SAc_2,$$

rms prismatic, often crossed, crystals, m. p. 142°, and its *benzoyl* derivative, $C_{14}H_{12}O_4SBz_2$, groups of radiating, prismatic ystals, m. p. 153—154°. When the sulphone is heated with romic acid in presence of water, an odour of *p*-benzoquinone is nitted, whilst oxidation with concentrated nitric acid yields :4:6-trinitrocresol.

β-m-*Hydroxytolylsulphone*, for which various constitutional rmulæ are proposed, crystallises with 1MeOH in shining, colourss prisms, m. p. 196—197°, and in a current of air sublimes unianged at 180—200°. The *diacetyl* derivative, $C_{14}H_{12}O_4SAc_2$, rms intergrown, prismatic crystals, m. p. 197°, and the *dibenzoyl* mpound, $C_{14}H_{12}O_4SBz_2$, microscopic, prismatic crystals, m. p. 24—225°.

Together with these two sulphones, the action of sulphuric acid 1 *m*-cresol yields 3-cresol-6-sulphonic acid and another cresollphonic acid, probably 3-cresol-2(or 4)-sulphonic acid, the *barium* $+H_2O$) and *potassium* ($+2\frac{1}{2}H_2O$) salts of which were analysed.

T. H. P.

Compounds of Bivalent Cobalt and Nickel with Catechol. [. R. F. Weinland and Anna Döttinger (*Zeitsch. anorg. Chem.*, 920, **111**, 167—174. Compare A., 1918, i, 298).—In an nalogous manner to that previously adopted, the authors have repared a basic sodium salt of cobalto-catechol of the formula $[Co(O{\cdot}C_6H_4O)_2]Na_2,3NaOH,14H_2O$. In the case of nickel, a basic ılt was not obtained, but two normal salts,

$$[Ni(O{\cdot}C_6H_4O)_2]Na_2,[Ni(O{\cdot}C_6H_4O)_3]Na_4,18H_2O,$$

1 thin, bluish-green leaflets, and $[Ni(O{\cdot}C_6H_4O)_2]Na_2,12H_2O$, in hick, dark green tablets. A further cobalt derivative of catechol obtained by heating a solution of cobalt acetate and catechol; his compound crystallises in blue needles, and has the formula $H_3{\cdot}CO_2{\cdot}Co{\cdot}O{\cdot}C_6H_4{\cdot}OH,H_2O$. Attempts to prepare a similar ickel derivative failed, but a green powder of the formula $Ii_3(C_6H_4O_2)_2(OH)_2,5H_2O$ was obtained.

J. F. S.

Tautomerism of Phenols. II.[§] Resorcinol. Walter Fuchs nd Benno Elsner (*Ber.*, 1920, **53**, [*B*], 886—898. Compare this ol., i, 159).—Resorcinol slowly reacts with a boiling aqueous soluion of sodium hydrogen sulphite, yielding a *substance*,

$$C_6H_9O_{11}S_3Na_3,$$

rhich, in all probability, is the sodium salt of the bisulphite comound of 3:5-diketo*cyclo*hexanesulphonic acid, the formation of rhich can be explained by the assumption that resorcinol reacts in s tautomeric form. It loses a molecule of sulphur dioxide almost nstantaneously, even in aqueous solution; a second molecule is liminated more slowly and with much greater difficulty, whilst he third molecule is only lost to a slight extent even after proracted treatment. When it is allowed to remain for some time

in contact with an aqueous solution of sodium hydroxide at t
ordinary temperature, it yields *sodium dihydroresorcinolsulphona*
colourless needles, which is freely soluble in water and does r
give precipitates with the salts of the heavy metals. With fer
chloride, an intense violet-red coloration is developed. It does n
show the usual reactions of resorcinol. It is oxidised by potassiu
permanganate to oxalic acid. It readily absorbs bromine, b
simultaneously becomes extensively decomposed, with formation
bromoform. *Dihydroresorcinolsulphonic acid* forms colourl
crystals, m. p. 172—175° (decomp.). The *barium* salt is al
described. Resorcinol is the main product of the fusion of t
latter with potassium hydroxide, whilst also sulphurous acid
removed. The constitution of the sulphonic acid has not be
definitely elucidated, but the reaction just described indicates th
the sulphonic group is in close proximity to a methylene grou
since it is otherwise difficult to explain how a dihydroxylated cyc
sulphonic acid could yield resorcinol with elimination of sulph
dioxide; it appears most probable that the acid has a symmetric
structure. H. W.

The Action of an Alcoholic Solution of Potassiu Hydroxide in the Presence of Zinc Powder on the Brom benzhydrols and on some of their Derivatives. P. Montagne (*Rec. trav. chim.*, 1920, **39**, 492—494).—When t bromobenzhydrols or their derivatives are boiled with an alcohol *solution of potassium hydroxide in the presence of zinc powder*, t bromine is completely replaced by hydrogen, but little or r resinous material is formed. W. G.

Polymorphism of Cholesterol Crystals. A. Richa (*Compt. rend. Soc. Biol.*, 1920, **83**, 389—391; from *Chem. Zent.* 1920, i, 896).—When a solution of cholesterol in hot acetic ac is evaporated, the substance is not infrequently deposited radiating clusters instead of long needles arranged in crosses; t transformation into rhombic plates by addition of a drop of alcoh does *not invariably occur*. H. W.

Preparation of Metacholesterol. Isaac Lifschütz (D.R.-P. 318900, 318901; from *Chem. Zentr.*, 1920, iv, 16).—I. Choleste or substances containing cholesterol are treated with mild oxidisi agents *until the formation of oxidation products of choleste* can just be detected by the acetic–sulphuric acid reaction. *Me cholesterol* forms silvery leaflets, m. p. 140—141°; it does not gi a coloration with ferric chloride or acetic–sulphuric acid. I acetyl and benzoyl derivatives also differ from those of cholester or oxycholesterol. *A solution of metacholesterol in alcohol*, aft addition of water and removal of alcohol by boiling, gives a pe fectly uniform, more or less opalescent, colloidal solution, whi can dissolve fats, higher alcohols, etc. Metacholesterol, wh melted to the extent of 2% with fats or oils or with vaselin, allo the addition of more than 500% of water.

II. Metacholesterol is obtained from animal matter containing cholesterol (i) by treating the cholesterol substances with solvents according to known processes, whereby the cholesterol is separated in the solid form, and by suitable treatment of the filtrates, preferably by concentration, precipitating metacholesterol, leaving practically only oxycholesterol in solution; (ii) by treating the mixture with volatile substances and water or with the latter alone, dialysing or filtering the liquid, and fractionating the dissolved matter for the purpose of removing the substances which have smaller power of uniting with water according to (i). Considerable amounts of metacholesterol are contained in ox brain, and more in the blood fat. The great capacity of metacholesterol of mixing with water makes it suitable for the preparation of ointments, cosmetics, emulsions, and similar fatty mixtures with a very high water content. H. W.

The Polyacid Salts of Monobasic Acids: Sodium Tribenzoate. PHILIPPE LANDRIEU (*Compt. rend.*, 1920, **170**, 1452—1454).—Benzoic acid gives an acid sodium salt having the composition $C_6H_5 \cdot CO_2Na, 2C_6H_5 \cdot CO_2H$, which crystallises in silky needles. W. G.

Hydrogen Persulphides. VI. Trisulphides and Tetrasulphides of certain Carboxylic Acids. IGNAZ BLOCH and MAX BERGMANN (*Ber.*, 1920, **53**, [*B*], 961—977. Compare A., 1911, *i*, 46, and previous abstracts).—*Acyl disulphides* may be readily prepared by the action of the requisite acid chloride on hydrogen disulphide in the presence of a small quantity of zinc chloride. In the case of fatty and fatty-aromatic acid chlorides, the trisulphides may be obtained in a similar manner, but with aromatic acid chlorides there is a marked tendency towards the shortening of the sulphur chain, with the production of disulphides, and this occurs to such an extent as to enable the crude hydrogen polysulphide to be advantageously used in the preparation of the latter. The aromatic trisulphides are readily prepared from sulphur dichloride and the potassium salt of the requisite thioacid ($2C_6H_5 \cdot CO \cdot SK + SCl_2 = 2KCl + S_3Bz_2$), and an extension of this method to sulphur monochloride affords a means of obtaining the tetrasulphides.

The acyl persulphides are, in general, colourless or faintly coloured crystalline substances, which are rather more stable than the hydrogen persulphides, but which, particularly in the cases of the higher sulphides, gradually decompose when preserved. The disulphides have already been extensively investigated; the reactions of the higher sulphides are closely similar to those of the disulphides, the additional sulphur which they contain being generally separated in the elementary state. The tri- and tetrasulphides show a marked tendency to eliminate sulphur and pass into the disulphides, and this action is particularly noticeable in the presence of feebly basic substances, which do not cause too extensive decomposition. Thus benzoyl tetrasulphide could be

degraded step by step by means of dimethylaniline, and benzoyl trisulphide was identified as the primary product of the change.

Acetyl trisulphide, S_3Ac_2, forms a greenish-yellow, viscous oil, D_4^{20} 1·3423, which becomes colourless at $-20°$, and can be frozen to a crystalline mass, leaflets or needles, m. p. $-19°$ to $-17°$. It could not be prepared in the pure condition. *Phenylacetyl trisulphide*, colourless, six-sided plates, has m. p. 85—86° after slight previous softening, and, with phenylhydrazine yields sulphur, hydrogen sulphide, and the phenylhydrazide of phenylacetic acid, m. p. 172—173°. Phenylacetyl disulphide, prepared from phenylacetyl chloride and hydrogen disulphide, has m. p. 60—61° (compare Johnson, A., 1906, i, 954). *Benzoyl trisulphide* forms prisms, m. p. 167—168° (corr.), but when crystallised from indifferent solvents is obtained in six-sided plates, which soften and partly melt at about 90°, resolidify, and again melt at 122—123° (corr.). The phenomenon appears to depend on polymorphism; conversion of the form of lower into that of higher melting point can be effected by crystallisation from mixtures of chloroform or carbon disulphide and light petroleum in the presence of sulphur chloride, whilst the reverse change is effected by the use of indifferent solvents. *Benzoyl tetrasulphide* forms almost colourless, flat prisms or broad leaflets, m. p. 83—84°, after very slight previous softening; it is converted by potassium thiobenzoate into benzoyl trisulphide, and, ultimately, benzoyl disulphide. *Anisoyl disulphide*, prepared from potassium thioanisate and oxidising agents or from crude hydrogen persulphide and anisoyl chloride in the presence of zinc chloride, crystallises in needles, m. p. 121—122° (corr.), and resembles benzoyl disulphide closely in its properties (the isolation of *potassium thioanisate* and of *thioanisic acid*, $OMe\cdot C_6H_4\cdot CO\cdot SH$, small, colourless needles, m. p. 82—83°, is described). *Anisoyl tetrasulphide* forms faintly coloured, microscopic needles, m. p. 104—105° (corr.), after slight softening. *Anisoyl trisulphide* closely resembles the benzoyl compound; when crystallised from chloroform in the presence of sulphur chloride, it has m. p. 168—169° (corr.), but, when obtained in the absence of the latter, the melting point is lower and very indefinite, marked softening usually occurring below 110°, and complete liquefaction between 150° and 160°. H. W.

The Action of Benzoyl Chloride on Potassium Sulphide. MAX BERGMANN (*Ber.*, 1920, **53**, [*B*], 979—984).—The action of molar proportions of potassium sulphide and benzoyl chloride in alcoholic solution is stated to lead to the formation of potassium thiolbenzoate, Ph·COSK, which is converted by a second molar proportion of benzoyl chloride into benzoyl sulphide. The reaction is found to follow a much more complex course when the sulphide and chloride are initially present in the molecular ratio, 1 : 2; benzoyl sulphide is only obtained in small amount, whilst the main products are benzoyl disulphide and a substance which can readily be separated from the latter by reason of its greater stability towards alcoholic ammonia and is regarded as *benzylidene*

bisthiobenzoate, CHPh(S·COPh)$_2$; it forms characteristic, moss-like masses of needles or prisms, m. p. 141° (corr.), and is readily decomposed by alcoholic alkali, but is stable to 1% alcoholic hydrogen chloride. The presence of the benzylidene group is proved by its conversion by hydrazine into benzylidenebenzoylhydrazine,

CHPh:N·NHBz,

m. p. 207—208° (corr.). Benzylidene bisthiobenzoate can also be prepared by the action of dry hydrogen chloride on a mixture of benzaldehyde and thiobenzoic acid, or, less advantageously, from benzylidene chloride and potassium thiobenzoate (2 mols.) in alcoholic solution. Benzylidene bisthiobenzoate reacts with piperidine in alcoholic solution to yield N-*thiobenzoylpiperidine*, CSPh·C$_5$NH$_{10}$, pale yellow plates, m. p. 63—64°, b. p. *ca.* 205°/12 mm. *Anisylidene bisthiobenzoate* forms prisms, m. p. 79—80°, to a cloudy liquid which becomes transparent at 81°; it does not appear to yield *N*-thiobenzoylpiperidine with piperidine. H. W.

Preparation of Chlorylsulphonamides. MAX CLAASS (D.R.-P. 318899; from *Chem. Zentr.*, 1920, iv, 14—15).—The sulphonamides of aromatic carboxylic acids are converted into the corresponding dichloryl compounds in the usual manner. The introduction of the carbonyl group into the nucleus increases the stability of the chlorylsulphonamides. *Dichlorylsulphonamidobenzoic acid*, from *p*-sulphonamidobenzoic acid and alkali hypochlorite solution and subsequent addition of acetic acid, has m. p. 203°. Sulphuric acid precipitates small amounts of *monochlorylsulphonamidobenzoic acid*, m. p. 223°, from the filtrate. H. W.

The Action of Diazoacetic Ester on Mesitylene. EDUARD BUCHNER and KARL SCHOTTENHAMMER (*Ber.*, 1920, **53**, [*B*], 865—873).—Previous investigations (A., 1911, i, 50, and earlier abstracts) have shown that aromatic hydrocarbons condense with ethyl diazoacetate with loss of nitrogen and formation of carboxylic esters of norcarane, and that the latter are transformed at elevated temperatures into derivatives of *cyclo*heptatriene. The primary addition appears to occur in such a manner that a quaternary carbon atom is never formed; the case of mesitylene, therefore, is of peculiar interest, since such a grouping must of necessity be present in the initial compound, if actually formed. It is found, however, that the product of the change is *ethyl trimethylcyclo*-*heptatrienecarboxylate*, which probably has the constitution

CMe·CH:CMe>C·CO$_2$Et.
‖
CH—CMe:CH

The action between mesitylene and ethyl diazoacetate is best carried out at 135—140°; the crude product, when distilled, gives a fraction, b. p. 137—143°/12 mm., which consists of ethyl trimethyl*cyclo*heptatrienecarboxylate mixed with ethyl fumarate. At 115—120°, reaction proceeds very slowly, but ultimately yields the same products; in the presence of copper powder, a brisk action

occurs, which leads almost exclusively to the formation of ethy fumarate. *Trimethylcycloheptatrienecarboxylic acid*, m. p. 142° is obtained by hydrolysis of the crude ester mixture, and is con verted by the successive action of phosphorus pentachloride and ammonia into the corresponding *amide*, long, colourless needles m. p. 151°. The acid unites readily with bromine, but the additive product is unstable and easily loses hydrogen bromide.

The first fractions obtained during the distillation of the crude ester give, when hydrolysed, a mixture of trimethyl*cyclo*heptatrienecarboxylic acid and mesitylacetic acid, m. p. 168°. The ester of the latter acid is also obtained by the protracted heating of ethyl trimethyl*cyclo*heptatrienecarboxylate at 200°, whilst the acid itself is formed when trimethyl*cyclo*heptanetricarboxylic acid is treated with glacial acetic acid and hydrogen bromide at the ordinary temperature. The action of bromine on mesitylacetic acid or trimethyl*cyclo*heptanetricarboxylic acid in warm glacial acetic acid solution yields *αα-dibromomesitylacetic acid*, $C_6H_2Me_3 \cdot CBr_2 \cdot CO_2H$, m. p. 249·5°.

In similar condensations, the formation of derivatives of β-phenylpropionic acid in small quantity has invariably been observed; this appears to be the case in the present instance also, since the action of alcoholic ammonia on the ester very slowly leads to the formation of mesitylacetamide and an *amide*, m. p. 118°, which, when hydrolysed, yields an *acid*, m. p. 46·5°, probably β-3:5-dimethylphenylpropionic acid; it could not be obtained in quantity sufficient for an extended investigation.

Trimethyl*cyclo*heptatrienetricarboxylic acid absorbs six atoms of hydrogen in glacial acetic acid solution in the presence of platinum and gives the oily *trimethylcycloheptanetricarboxylic acid*, which is stable towards permanganate, and is characterised by conversion into the corresponding *amide*, long needles, m. p. 148°. H. W.

Melting Point of Salicylic Acid. W. J. BUSH & Co., LTD. (*Perfumery and Essent. Oil Rec.*, 1920, **11**, 207).—Pure salicylic acid melts at 159°, and m. p. of 158° to 159° are regularly obtained with commercial samples of British salicylic acid. The m. p. 156—157°, quoted in the pharmacopœia and commonly accepted, is consequently considerably too low. G. F. M.

Molecular Compounds of Inorganic Haloids. VII. Hydroxycarboxylic Acid Titanates, Polyphenol Titanates, and certain Allied Compounds. ARTHUR ROSENHEIM and OTTOKAR SORGE (*Ber.*, 1920, **53**, [*B*], 932—939).—A further extension of previous work (compare A., 1915, i, 537, and previous abstracts). *Titanitrisalicylic acid*, $C_6H_4<^{O}_{CO_2}>Ti(O \cdot C_6H_4 \cdot CO_2H)_2$, is obtained when the hydrochloride of chlorotitanitrisalicylic acid,

$$TiCl(O \cdot C_6H_4 \cdot CO_2H)_3,$$

is exposed to the air; the *pyridinium*, *ammonium*, *sodium*, and *potassium* salts are described.

Titanidisalicylate, $Ti\left(\begin{matrix}O\cdot C_6H_4 \\ O\cdot CO\end{matrix}\right)_2$ (*loc. cit.*), is converted by pyridine in alcoholic solution into the salt

$$TiO(O\cdot C_6H_4\cdot CO_2\cdot C_5H_6N)_2;$$

the corresponding *ammonium* and *mercuric* salts have been investigated.

Titanium chloride reacts with a solution of phenyl salicylate in anhydrous ether to yield the *compound* $[Ti(O\cdot C_6H_4\cdot CO_2Ph)_3]_2TiCl_6$; with salicylamide, under the same conditions, a brown, smeary mass is obtained, which evolves hydrogen chloride and gives $[TiCl(O\cdot C_6H_4\cdot CO\cdot NH_2)_3],HCl$; an alcoholic solution of the latter deposits the *compound* $TiCl(O\cdot C_6H_4\cdot CO\cdot NH_2)_3,EtOH$.

The behaviour of *m*-cresotic acid closely resembles that of salicylic acid. Thus, the purple compound,

$$TiCl(O\cdot C_6H_3Me\cdot CO_2H)_3,HCl,$$

passes, on exposure to air, into the yellowish-white *acid*,

$$C_6H_3Me{<}\begin{matrix}O- \\ CO_2\end{matrix}{>}Ti(O\cdot C_6H_3Me\cdot CO_2H)_2,$$

the *pyridinium* and *ammonium* salts of which are described. The acid is converted by heat into titanium basic *m*-cresotate,

$$Ti\left({<}\begin{matrix}O\cdot C_6H_3Me \\ O\cdot CO\end{matrix}\right)_2$$

which is transformed by alcohol and pyridine into the yellow *salt*, $TiO(O\cdot C_6H_3Me\cdot CO_2\cdot C_5H_6N)_2$; the corresponding *ammonium* and *potassium* salts are described.

Other hydroxycarboxylic acids appear to react in an analogous manner with titanium chloride; the salts derived from protocatechuic, gallic, and pyrogallolcarboxylic acids were, however, too soluble to permit their isolation in the pure state.

In the compounds which have been described so far, the hydroxyl group is, from the point of view of the co-ordination theory, equivalent to the carboxyl group. It is, therefore, not surprising to find that the polyphenols yield complexes with titanium tetrachloride. Thus, when ethereal solutions of catechol and titanium chloride are mixed, a vigorous action occurs, the primary product of which could not be isolated; if, however, the ether is removed and the residue treated with aqueous ammonia, the *ammonium* salt, $C_6H_4{<}\begin{matrix}O \\ O\end{matrix}{>}Ti(O\cdot C_6H_4\cdot ONH_4)_2,H_2O$, is obtained (the corresponding *potassium* and *silver* salts are described). Other chlorides behave similarly. Thus, silicon tetrachloride and catechol give colourless, very unstable crystals of *tricatechol silicon chloride* (?), which are converted by alcoholic ammonia into *ammonium tricatechol silicate*, $C_6H_4O_2{:}Si(O\cdot C_6H_4\cdot ONH_4)_2$, and by alcoholic pyridine into the corresponding *pyridinium* salt. Similarly, zirconium oxychloride and thorium nitrate react with a boiling aqueous ammoniacal solution of catechol to yield the *salts*, $C_6H_4O_2{:}Zr(O\cdot C_6H_4\cdot ONH_4)_2,7H_2O$ and $C_6H_4O_2{:}Th(O\cdot C_6H_4\cdot ONH_4)_2,7H_2O$.

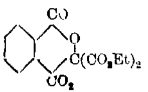
Titanium chloride reacts readily with pyrogallol in ethereal solution, and the product obtained after removal of the solvent is transformed by aqueous ammonia into the *salt*,

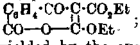
$$OH{\cdot}Ti[O{\cdot}C_6H_3(OH){\cdot}ONH_4]_3,3H_2O.$$

H. W.

The Constitution of Phthalylmalonic Esters and Allied Substances. JOHANNES SCHEIBER and GEORG HOPFER (*Ber.*, 1920, **53**, [*B*], 898—913).—Recent spectrochemical observations (A., 1918, i, 436) have led Auwers and Auffenberg to cast doubts on the correctness of the formula, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C(CO_2Et)_2$ (I), assigned to phthalylmalonic ester by Scheiber (A., 1912, i, 559), and to revert to the older formula, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{O}>C{:}C(CO_2Et)_2$ (II). The problem has now been re-investigated by examining the action of ozone on the ester and a number of related compounds.

A substance of formula (II) would be expected to react witl ozone to give an ozonide which would be decomposed by cold wate with the formation of phthalic acid and ethyl mesoxalate; th *accumulation of negative substituents around the double bon* would not inhibit this reaction, since it is found that the similarl constituted benzylidenephthalide yields phthalic acid and benz aldehyde, whilst benzylidenemalonic acid gives benzaldehyde o benzoic acid and mesoxalic acid, and α-cyanocinnamic ester yield benzaldehyde or benzoic acid and the semi-nitrile of mesoxalic este (*phenylhydrazone*, silky leaflets, m. p. 181°). Actually, eth phthalylmalonate is only slowly attacked by ozone at −20° an yields small amounts of phthalic acid and ethyl mesoxalate, bu the main product (about 80%) is an oily substance (this occasionall solidifies to a colourless mass, m. p. about 48°, which cannot b further purified), which is characterised by its unusual stabili towards water and appears to be a peroxide, probably having t annexed formula. Hydrolysis of the latt in so far as it can be effected by water, lea to the production of phthalic acid and eth mesoxalate, and this doubtless accounts for portion of these substances which are fou after ozonisation of phthalylmalonic est The results of the experiments, therefore, te



to confirm the symmetrical structure of the ester, and the appare discordance between the authors' conclusions and those of Auw and Auffenberg are ascribed to the dissimilarity of the experimen conditions and to the possibility of desmotropic change. It appe that the solid ester has the constitution (I), and, in the molt or dissolved state, passes more or less completely into the for (II) or (III),  ; indications of the presence the latter are yielded by the evolution of carbon dioxide dur ozonisation.

Very similar observations are recorded with succinylmalonic ester, which, after ozonisation and treatment of the product with water, is found to give small quantities of succinic acid and ethyl mesoxalate, the main product, however, being a *diperoxide* characterised by great stability towards water. The solid ester, therefore, appears to have the symmetrical constitution and to undergo desmotropic change when melted or dissolved.

When similarly treated, the two ethyl phthalylacetoacetates yield phthalic acid, acetic acid, and ethyl glyoxylate, but whereas the ester of lower melting point gives the products in quantitative amount, that of higher melting point only gives them in 60% yield. The constitution of the former is without doubt expressed by the formula $\begin{matrix} C_6H_4\cdot CO\cdot C\cdot CO_2Et \\ CO—O—CMe \end{matrix}$, whilst the latter in all probability has the constitution $C_6H_4<^{CO}_{CO}>C<^{COEt}_{COMe}$; in any case, the structure $CO<^{C_6H_4}_{-O-}>C<^{COMe}_{CO_2Et}$ is definitely excluded, since such a compound would yield phthalic acid and ethyl $\alpha\beta$-diketobutyrate, the latter of which is not produced.

The results of ozonisation do not completely confirm the constitutions previously ascribed to the phthalylbenzoylacetones; the smooth conversion of the isomeride of lower melting point into phthalic acid and phenyl methyl triketone indicates that it has the formula $CO<^{C_6H_4}_{-O-}>C<^{COMe}_{COPh}$. The constitution of the isomeride of higher melting point has not been definitely elucidated, but the present investigation accentuates the improbability that the compounds are stereoisomerides.

Phthalylacetylacetone yields phthalic acid, methylglyoxal, and acetic acid, thus confirming the structure, $CO<^{C_6H_4\cdot CO}_{O—CMe}>C\cdot COMe$, assigned to it previously. H. W.

[Formation of Iron Tannates.] C. A. Mitchell (*Analyst*, 1920, **45**, 254—256).—When solutions of ferrous salts and gallotannic acid are mixed, a pale ferrous tannate appears to be formed, any ferric salt present being immediately reduced to the ferrous condition. When this solution of ferrous tannate is exposed to the air, it is slowly oxidised, and yields insoluble incrustations and deposits. The earlier precipitates contain a proportion of iron (for example 5·38—5·75%) corresponding with Wittstein's iron tannate, $Fe_2(C_{14}H_9O_9)_6$ (*Jahresber. Chem.*, 1848, **28**, 221). As the oxidation proceeds, the successive deposits contain more iron, and finally approximate in composition to the precipitate which Pelouze (*Ann. Chim. Phys.*, 1833, [ii], **54**, 337) obtained by exposing a solution of ferric sulphate and gallotannic acid to the air for a month, namely, $^{C_{14}H_8O_9}_{C_{14}H_9O_9}>Fe\cdot Fe<^{C_{14}H_8O_9}_{C_{14}H_9O_9}$, which contains 8·4% of iron. This compound, however, is not formed at

first from ferric sulphate, but the presence of ferric salts in the solution promotes the oxidation to the more highly oxidised compounds. The addition of a small amount of hydrogen peroxide to a solution of ferrous tannate causes the precipitation of a tannate containing iron, corresponding with the amount (14·21%) in Wittstein's tannate, $C_{14}H_9O_9{\overset{O}{>}}Fe{\cdot}Fe{\overset{O}{<}}C_{14}H_9O_9$. If a large amount of hydrogen peroxide is added, a heavy precipitate containing 21 to 24% of iron is immediately formed. This approximates in composition to Ruoss's basic tannate, $(C_{14}H_7O_9)(FeO)_2$, with 24·42% of iron (*Zeitsch. anal. Chem.*, 1902, **41**, 732). Neither of these compounds, however, appears to be formed in the atmospheric oxidation of ferrous tannate. By adding a few drops of pine oil to a ferrous tannate solution, a dense precipitate containing about 8·1% of iron is obtained. A similar catalytic acceleration of the oxidation to Pelouze's tannate is effected by the addition of saliva, but in this case the action proceeds much more slowly. C. A. M.

Manufacture of Hydroxyaldehydes and their Ethers. ANDRE WEISS (Brit. Pat. 139153).—Aromatic hydroxyaldehydes or their ethers are obtained by the interaction of a phenol or phenol ether with formaldehyde and an aromatic nitroso-compound such as nitrosobenzene, *p*-nitrosodimethylaniline, etc. For example, vanillin is obtained in excellent yield by heating for several hours on a water-bath a mixture of guaiacol (1 mol.), formaldehyde (1 mol.), and *p*-nitrosodimethylaniline (½ mol.), methyl or ethyl alcohol being added as a diluent, and hydrogen chloride being bubbled through continuously. *p*-Aminodimethylaniline is formed as a by-product, and is removed by extraction with benzene or ether after rendering alkaline with sodium hydroxide and distilling off the alcohol. The liquor is then acidified and the vanillin extracted with benzene and purified by distillation in a vacuum. G. F. M.

Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXVI. The Binary Systems of Acetophenone and Benzophenone, respectively, with Phenols and their Derivatives. ROBERT KREMANN and HERMANN MARKTL (*Monatsh.*, 1920, **41**, 43—75. Compare this vol., i, 564).—Freezing-point curves have been constructed for the binary systems, acetophenone with *a*-naphthol, *β*-naphthol, catechol, quinol, resorcinol, pyrogallol, phenol, *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, 2:4-dinitrophenol, and picric acid respectively, and for benzophenone with picric acid and 2:4-dinitrophenol. It is shown that both *a*-naphthol and *β*-naphthol form an equimolecular compound with acetophenone, melting at 13° and 8° respectively. The three dihydroxybenzenes each form an equimolecular compound with acetophenone, which melts as follows: quinol, 40°; resorcinol, 13°; catechol, 1°. Pyrogallol forms two compounds with acetophenone, one molecule of acetophenone

phenone combining with one half and one molecule of pyrogallol respectively, and the compounds melting at 18·5° and 21°. It is shown that the *equimolecular compound* with *catechol* is very much more dissociated in the fused mass than that with resorcinol. Benzophenone forms no compounds with any of the substances used; here simple eutectics are formed, as follows: at 35°, with 20% of 2:4-dinitrophenol, and at 27° with 29% of picric acid. Acetophenone forms no compounds with the nitrophenols or with 2:4-dinitrophenol; here, again, simple eutectics are formed as follows: at 2·5°, with 47% of *o*-nitrophenol; at −16°, with 41·5% of *m*-nitrophenol; at −4°, with 38% of *p*-nitrophenol; at 12°, with 21% of 2:4-dinitrophenol. In the case of picric acid, an *equimolecular compound* between *acetophenone* and *picric acid*, and a further compound between two molecules of acetophenone and one molecule of picric acid, m. p. 50°, are formed. J. F. S.

Asymmetric Synthesis. RICHARD WEISS (*Monatsh.*, 1919, **40**, 391—402).—The interaction of phenyl-*p*-tolylketen and *l*-menthol in absolute ethereal solution yields *l*-menthyl *d*-phenyl-*p*-tolylacetate. This reaction represents an asymmetric synthesis, since an optically active compound is formed from an optically inactive one without the intermediate formation of the racemic compound. According to the author's results, the *l*-menthyl *d*-phenyl-*p*-tolylacetate described by McKenzie and Widdows (T., 1905, **107**, 702) was partly racemised.

Dibromobenzyl p-*tolyl ketone*, $CBr_2Ph{\cdot}CO{\cdot}C_6H_4Me$, crystallises in yellow prisms, m. p. 127·5—128°, and yields *p*-toluic acid when fused with potassium hydroxide. When heated with alcohol in a sealed tube at 140—160°, it gives:

4-Methylbenzil, $COPh{\cdot}CO{\cdot}C_6H_4Me$, which forms crystals, m. p. 99—101°, and distils unchanged in a vacuum. Since the action of hydrazine on an alcoholic solution of 4-methylbenzil yields only a small proportion of a crystalline substance, together with much syrupy material incapable of purification, the preparation of the phenyl-*p*-tolylketen was carried out by way of phenyl-*p*-tolylglycollic acid.

Phenyl-p-*tolylglycollic acid*, $OH{\cdot}CPh(C_6H_4Me){\cdot}CO_2H$, prepared by heating 4-methylbenzil with potassium hydroxide solution at 150—160°, forms crystals, m. p. 131—133°, and is coloured blood-red by concentrated sulphuric acid.

a-Chlorophenyl-p-*tolylacetyl chloride*, $C_6H_4Me{\cdot}CPhCl{\cdot}COCl$, prepared by the method used by Staudinger for *a*-chlorodiphenylacetyl chloride (*Annalen*, 1907, **356**, 72), forms a yellow oil, which is decomposed with moderate rapidity by atmospheric moisture.

l-*Menthyl* d-*phenyl*-p-*tolylacetate*,

$$C_6H_4Me{\cdot}CHPh{\cdot}CO_2{\cdot}CH{<}{\begin{matrix}CH_2{\cdot}CHMe\\CHPr^{\beta}{\cdot}CH_2\end{matrix}}{>}CH_2,$$

prepared by reducing *a*-chlorophenyl-*p*-tolylacetyl chloride with zinc turnings under ether and in an atmosphere of carbon dioxide, and treating the phenyl-*p*-tolylketen thus formed with *l*-menthol,

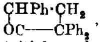
forms a yellow, viscous oil, b. p. 190—196°/1 mm., $[\alpha]_D$ in acetone $-45.40°$. The ester is accompanied by a small proportion of phenyl-*p*-tolylacetic acid, due to the action of water on the keten.

The phenylacetic acid used for the synthesis of the benzyl *p*-tolyl ketone was prepared by converting benzyl chloride into benzyl cyanide and hydrolysing the latter, and was found to be mixed with a little *phenylacetobenzylamide*, $CH_2Ph·CO·NH·CH_2Ph$, which may also be obtained by the Schotten-Baumann reaction from benzylamine and phenylacetyl chloride, and forms crystals, m. p. 122°. This compound is formed in accordance with the following scheme: $CH_2Ph·CN + CH_2PhCl \longrightarrow CH_2Ph·CCl:N·CH_2Ph \longrightarrow CH_2Ph·C(OH):N·CH_2Ph \longrightarrow CH_2Ph·CO·NH·CH_2Ph$.

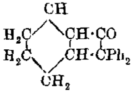
T. H. P.

The Action of an Alcoholic Solution of Potassium Hydroxide in the Presence of Zinc Powder on the Bromobenzophenones and on some of their Derivatives. P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 483—491).—Bromobenzophenones and their derivatives when boiled in an alcoholic solution of potassium hydroxide with zinc powder are reduced to benzhydrols, but, at the same time, the bromine is completely replaced by hydrogen, and a certain amount of resinous material is formed. W. G.

Ketens. XXXI. *cyclo*Butanedione Derivatives and the Polymeric Ketens. H. STAUDINGER (*Ber.*, 1920, **53**, [*B*], 1085—1092).—It has recently been suggested by Schroeter (A., 1917, i, 145) that the polymeric ketens are molecular compounds instead of *cyclo*butane derivatives, as postulated by Staudinger. The author does not agree with this view, and, in the present communication, gives a survey of the literature of this class of substances, in which it is shown that their properties can be adequately interpreted by the *cyclo*butane formulation. New experimental evidence is not brought forward. H. W.

Ketens. XXXII. *cyclo*Butane Derivatives from Diphenylketen and Ethylene Compounds. H. STAUDINGER and E. SUTER [and, in part, R. FLATT, H. W. KLEVER, KARL KNOCH, and E. STANDT] (*Ber.*, 1920, **53**, [*B*], 1092—1105).—Diphenylketen readily condenses with styrene, yielding 1 : 1 : 3-*triphenyl*cyclo*butane*-2-*one*, , colourless needles, m. p. 135—136°, from which the initial products are regenerated by heating at about 200°. The substance could not be caused to yield an oxime, semicarbazone, or phenylhydrazone, nor did it condense with benzaldehyde in the presence of alkali. When treated with methyl-alcoholic sodium hydroxide solution, it gives $\alpha\alpha\gamma$-*triphenyl*-n-*butyric acid*, white powder, m. p. 178—179° (*methyl* ester, m. p. 125—126°), which is converted at 260° into styrene and diphenylacetic acid. Similarly, diphenylketen and *p*-methylstyrene give 1 : 1-*diphenyl*-3-p-*tolyl*-cyclo*butane*-2-*one*, colourless needles, m. p. 117°, which is decomposed into its constituents by heat, and with alkali gives

αα-diphenyl-γ-p-tolyl-n-butyric acid, white powder, m. p. 207°. p-*Chlorostyrene*, b. p. *ca.* 74°/12 mm., is prepared by the action of magnesium methyl iodide on *p*-chlorobenzaldehyde and subsequent dehydration of the carbinol so formed by heating it with potassium pyrosulphate; the yields are poor (30%), on account of the readiness with which polymerisation occurs. With diphenylketen, the substance yields 1:1-*diphenyl*-3-p-*chlorophenyl*cyclo*butane*-2-*one*, crystalline powder, m. p. 120—121°, from which *αα-diphenyl-γ-p-chlorophenyl-n-butyric acid*, m. p. 178—179°, is obtained in the usual manner. Similarly, 1:1-*diphenyl*-3-p-*anisyl*-cyclo*butane*-2-*one*, m. p. 77—78°, is prepared from *p*-methoxystyrene. Vinyl ethyl ether unites with diphenylketen to form 1:1-*diphenyl*-3-*ethoxy*cyclo*butane*-2-*one*, crystalline powder, m. p. 71—72°, which is relatively unstable and decomposes into its constituents when gently heated, and, apparently, when preserved; it is converted by alcoholic alkali into an acid, m. p. about 116°. Tetrahydrobenzene and diphenylketen yield a *substance* (annexed formula), colourless needles, m. p. 129—130°, which is transformed by alkali into *diphenyl*cyclo*hexylacetic acid*, crystalline powder, m. p. 122°. *cyclo*Pentadiene and diphenylketen unite readily in molar proportions, giving the *compound* I or II, m. p. 89—90°, which is readily resolved by heat into



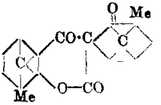
(I.) (II.)

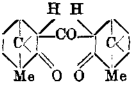
its components, and with alkali gives the corresponding *acid*, m. p. 125°. The substance is readily reduced to the corresponding saturated *compound*, colourless needles, m. p. 92°, which decomposes when heated into diphenylketen and *cyclo*pentene. Diphenylketen unites similarly with phenylmethylfulvene to yield a *product*, m. p. 168—169°. Unlike the previous cases, *N*-methylpyrrole unites with two molecules of diphenylketen even when the substances are used in molar proportions; the product is a white, crystalline powder, m. p. *ca.* 200° (decomp.) after softening at 190°. Pyrrole itself yields N-*diphenylacetylpyrrole*, m. p. 122°. *as*-Diphenylethylene gives 1:1:3:3:5:5-*hexaphenyl*cyclo*hexane*-2:4-*dione*, m. p. 180—181°, which yields *ααγγεε-hexaphenyl-δ-ketohexoic acid*, needles, m. p. 121—123°. H. W.

Ketens. XXXIII. Attempts to Prepare Optically Active Ketens. H. Staudinger and S. Schotz (*Ber.*, 1920, **53**, [*B*], 1105—1124).—The investigation was undertaken in the hope that the isolation of an optically active keten would greatly facilitate the investigation of the rate at which these substances unite with various compounds by allowing the course of the reaction to be followed polarimetrically. The present communication describes the efforts to obtain certain camphorketens. Unfortunately, the

substances are too unstable to permit their isolation in the unimolecular form, but various dimerides have been obtained and characterised as *cyclo*butane derivatives. The fact that in certain instances stereoisomerides can be isolated is further evidence against Schroeter's conception of the substances as additive products.

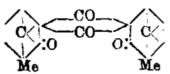
Camphorcarboxylic chloride is most conveniently prepared by the action of thionyl chloride at the ordinary temperature on the corresponding acid. When heated, it loses hydrogen chloride rapidly at 170°, slowly, but with the production of a purer product, at 100°, and passes into the pyronone derivative (annexed formula), needles, m. p. 196°, $[\alpha]_D$ +293·8° in benzene, +302·2° in ethyl acetate solution, which is identical with the product obtained by Kachler and Spitzer by the action of acetyl chloride on camphorcarboxylic acid. Attempts to depolymerise the substance were unsuccessful. When subjected to the prolonged action of concentrated hydrochloric acid at the ordinary temperature, the dimeride is transformed into the corresponding hydroxy-acid, m. p. 262° (Kachler and Spitzer give m. p. 264°), which, when heated at about 290°/0·1 mm., is reconverted into the substance, m. p. 196°, a little camphor being simultaneously formed. The acid is very sensitive towards alkali, and is converted by aqueous potassium hydroxide into the *ketone* (annexed formula), m. p. 180°.

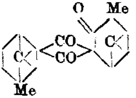




Attempts were made to prepare camphorketen from bromocamphorcarboxyl bromide (the latter, m. p. 80—81°, is obtained by the action of bromine in the presence of carbon disulphide on camphorcarboxyl chloride, removal of the halogen acids from the solution by carbon dioxide, and subsequent treatment of the solution with hydrogen bromide); the bromide reacts readily with zinc in ethereal solution, but yields only the acid, m. p. 264°, and the pyronone compound, m. p. 196° (see above).

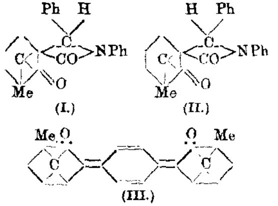
Camphorcarboxyl chloride readily loses hydrogen chloride under the influence of basic reagents, particularly quinoline, and the resultant solution contains *camphorketen* in the free state for a short period. Polymerisation, however, readily results, with the formation of a mixture of cis- and trans-*dicamphor*cyclo*butanediones* (I and II); the former has m. p. 152—153°, $[\alpha]_D$ +116·3° in benzene,

(I.) 

(II.) 

+126·8° in ethyl acetate solution, whilst the latter has m. p. 150—151°, $[\alpha]_D$ +61·1° in benzene, +62·9° in ethyl acetate. When

either polymeride is heated for a short time at 160—170°, the keten is transitorily formed, which rapidly passes into the pure product of m. p. 196°. With *p*-toluidine, either substance gives camphorcarboxyl-*p*-toluidide, whilst with hydrochloric acid the same acid is obtained as from the pyronone derivative; with methyl alcohol and alkali, *methyl camphorcarboxylate*, b. p. 143—145°/12 mm., 142°/13 mm., $[\alpha]_D$ +57·91° in ethyl acetate solution, is obtained. With ethyl-alcoholic potassium hydroxide solution, the reaction follows a different course, yielding small amounts of a new *acid*, m. p. about 187°, but neither camphorcarboxylic acid nor its ethyl ether; the main product is dicamphorketone, m. p. 182° (see above), which is more conveniently prepared by the action of dilute aqueous sodium hydroxide on an ethereal solution of either polymeride.



(I.) (II.)

(III.)

The formation of camphorketen from the *cyclo*butanedione derivative is established, not only by the appearance of coloration, but also by addition of certain reagents, which combine so rapidly with the keten that combination occurs before polymerisation can take place. Thus, for example, the dicamphor*cyclo*butanediones readily react with benzylideneaniline to yield the two stereoisomeric *β-lactams* (I and II), m. p.'s 166·5° and 195—196° respectively, and with *p*-benzoquinone to give *dicamphorquinodimethane* (III), orange-coloured crystals, m. p. 305—306°. H. W.

The Chloroquinones. A. J. DEN HOLLANDER (*Rec. trav. chim.*, 1920, **39**, 481—482).—The author has repeated the work of Peratoner and Genco (A., 1895, i, 342) and of Oliveri Tortorici (A., 1898, i, 303) on the preparation of 2 : 3-dichloro-*p*-benzoquinone. He found no evidence of the formation of this compound, the products he obtained being 2 : 5-*dichloro-p*-benzoquinone and 2 : 6-dichloro-*p*-benzoquinone. W. G.

The Fission of certain Glucosides and Amygdalin. GÉZA ZEMPLÉN (*Ber.*, 1920, **53**, [*B*], 996—1006).—Amygdalin is known to contain a biose which is hydrolysed by acids or by emulsin to two molecules of dextrose, but its identity has not been further established. The experiments now described were undertaken in the hope that hepta-acetylamygdalin might undergo fission under the influence of a solution of hydrogen bromide in glacial acetic acid in such a manner as to yield phenylbromoacetonitrile and the acetylbromo-compound of the biose of amygdalin. The feasibility of this plan is shown by experiments with a number of acetylated

cellobiosides, but, unfortunately, the process proves not to be available for amygdalin, in which the presence of the cyanogen group renders the glucosidic union between mandelic acid and the biose more stable than the ethereal bond between the two glucose residues. Attempts to avoid this difficulty by using hepta-acetyl-amygdalinic acid were unsuccessful, and it was further not found possible to obtain a suitable crystalline derivative of amygdalin which was free from nitrogen.

Hepta-acetylbenzylcellobioside, $CH_2Ph\cdot O\cdot C_{12}H_{14}O_{10}Ac_7$, long, colourless, silky needles, m. p. 193° after softening at 190°, $[\alpha]_D^{20}$ $-37\cdot4°$ in chloroform solution, is prepared by the interaction of acetylbromocellobiose and benzyl alcohol in benzene solution in the presence of silver carbonate, and is hydrolysed by hydrogen bromide in glacial acetic acid to acetylbromocellobiose, m. p. about 190° (decomp.), $[\alpha]_D^{20}$ $+92\cdot0°$ in chloroform solution. Under similar conditions, the latter substance was also obtained from *hepta-acetylmethylcellobioside*, small, colourless needles, m. p. 180°, from *hepta-acetyl*iso*butylcellobioside*, slender, colourless needles, m. p. 196—197°, $[\alpha]_D^{15}$ $-21\cdot5°$ in chloroform solution, and from *hepta-acetylphenylcellobioside*, yellowish-grey needles, m. p. 193° (prepared from phenol and acetylbromocellobiose in the presence of quinoline). Tetra-acetyl-β-methylglucoside appeared to undergo fission in a similar manner, since, although acetylbromoglucose could not be isolated in the crystalline state, its presence could be deduced from the abundant formation of phenylglucosazone after hydrolysis of the product with calcium carbonate and subsequently with aqueous alcoholic alkali. On the other hand, tetra-acetylsalicin yielded *tetra-acetylsalicin bromide*, $CH_2Br\cdot C_6H_4\cdot O\cdot C_6H_7O_5Ac_4$, long, colourless prisms, m. p. 167°, $[\alpha]_D^{15}$ $+47\cdot1°$ in chloroform solution, the free hydroxyl groups of the saligenin residue being replaced by bromine.

Tetradeca-acetyldiamygdalinimide,

$$(C_{17}H_{14}O_{10}Ac_7\cdot O\cdot CHPh\cdot CO)_2NH,$$

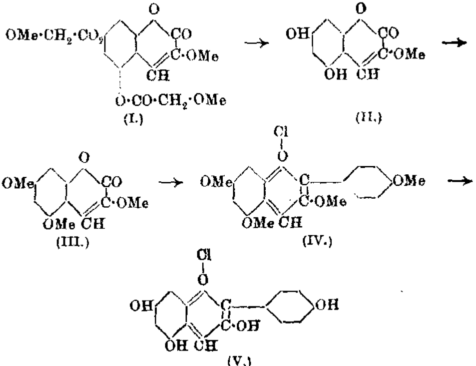
is prepared by saturating a solution of hepta-acetylamygdalin in chloroform containing a little absolute alcohol with dry hydrogen chloride; it forms long needles, m. p. 212°, $[\alpha]_D^{21}$ $-72\cdot1°$ in chloroform solution. It is hydrolysed by alcoholic potassium hydroxide solution to *diamygdalinimide*, which is hydrolysed by boiling aqueous hydrochloric acid with abundant production of dextrose.

H. W.

Action of Light on Colloidal Chlorophyll in the Presence of Stabilising Agents. RENÉ WURMSER (*Compt. rend. Soc. Biol.*, 1920, **83**, 437—438; from *Chem. Zentr.*, 1920, i, 895).—Colloidal chlorophyll, prepared according to the directions of Willstätter and Stoll, is much more sensitive to light than the natural product. This sensitiveness can be greatly depressed by certain colloids, of which gelatin appears to be the most potent; white of egg and gum arabic are much less powerful, whilst starch is inactive. Possibly an action of salts on the complex may be observed in plants. If the effect of the protective colloid is due to shielding

from oxygen, the same effect may possibly be expected from carbon dioxide. H. W.

Synthesis of Pelargonidine. Richard Willstätter and László Zechmeister (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, **34**, 886—893).—The condensation of 2:4:6-trihydroxybenzaldehyde with sodium methoxyacetate and methoxyacetic anhydride at 150—155° gives 5:7-*dimethoxyacetyl-3-methoxycoumarin* (I), prisms, m. p. 170—171° (corr.), from which, by treatment with cold dilute sodium hydroxide solution, 5:7-*dihydroxy-3-methoxycoumarin* (II), prisms or rhombic leaflets, m. p. 280—285° (corr.; decomp.), is obtained. 3:5:7-*Trimethoxycoumarin* (III), prisms or oblong leaflets, m. p. 171—172° (corr.), formed from the latter by treatment with diazomethane, reacts with excess of magnesium anisyl bromide, the product giving 3:5:7-*trimethoxy*-2-p-*anisylpyrylium chloride* (IV), bluish-red prisms (compare Decker and Fellenberg, A., 1907, i, 1064), from which the methyl groups are removed by means of boiling hydriodic acid in presence of phenol. 3:5:7-Trihydroxy-2-*p*-hydroxyphenylpyrylium *iodide* thus obtained gives a corresponding *chloride* (V), identical in composition, crystalline form, solubility, reaction, and absorption spectrum with the chloride of natural pelargonidine (Willstätter and Bolton, A., 1914, i, 564; 1915, i, 283).



J. K.

Chromanones. II. The Brazilin and Hæmatoxylin Question. P. Pfeiffer and H. J. Emmer (*Ber.*, 1920, **53**, [*B*], 945—953).—A further contribution to the synthesis of substances

llied to brazilin and hæmatoxylin (compare Pfeiffer and Grimmer ., 1917, i, 661).

7-Methoxychromanone [7-methoxy-2 : 3-dihydro-γ-benzopyrone] ondenses with vanillin methyl ether in alcoholic solution in the resence of sodium hydroxide to yield *7 : 3′ : 4′-trimethoxy-3-benzylidene-2 : 3-dihydro-γ-benzopyrone*, almost colourless needles, m. p. 39—140°, which is reduced by hydrogen in the presence of latinum black to *7 : 3′ : 4′-trimethoxybenzylchroman* [*7 : 3′ : 4′-trimethoxy-3-benzyl-2 : 3-dihydro-γ-benzopyrone*],

$$OMe\cdot C_6H_3<\begin{matrix}O—CH_2\\ CO\cdot CH\cdot CH_2\cdot C_6H_3(OMe)_2\end{matrix},$$

olourless, shining needles, m. p. 87°. Similarly, 7-methoxyhromanone condenses with piperonal to give the *piperonylidene* lerivative, pale yellow, felted needles, m. p. 149°, and with urfuraldehyde to yield the *furfurylidene* compound, needles, m. p. 19—120°.

7 : 8-Dimethoxychromanone [*7 : 8-dimethoxy-2 : 3-dihydro-γ-benzopyrone*], colourless leaflets, m. p. 100—101°, is obtained by the eduction of the corresponding chromone with hydrogen in the resence of platinum black; it yields a *semicarbazone*, colourless ieedles, m. p. 218° (decomp.), an *oxime*, long, shining needles, n. p. 152°, a *piperonylidene* derivative, small, pale yellow needles, n. p. 181°, and a *furfurylidene* compound, pale yellow needles, n. p. 133°. Attempts to condense the chromanone with vanillin nethyl ether met with difficulty, but a *substance*, slender, yellow ieedles, m. p. 133—134°, which is probably 7 : 8 : 3′ : 4′-tetranethoxy-3-benzylidene-2 : 3-dihydro-γ-benzopyrone, was isolated in mount too small for identification.

Gallacetophenone dimethyl ether condenses with piperonal in the resence of alcohol and warm 50% aqueous sodium hydroxide olution yielding *piperonylidenegallacetophenone dimethyl ether*, $OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH:CH\cdot C_6H_3:O_2:CH_2$, deep yellow needles, m. p. 178° (*perchlorate*, dark violet crystals; *acetyl* derivative, yellow leaflets, m. p. 127°), and with furfuraldehyde to give *furfurylidenegallacetophenone dimethyl ether*, golden-yellow needles or leaflets, m. p. 105° (*acetyl* derivative, m. p. 92°). H. W.

Tannins. IV. Hamameli-tannin. II. KARL FREUDENBERG and DANIEL PETERS (*Ber.*, 1920, **53**, [*B*], 953—961).—Further investigation has confirmed the previous conclusion (A., 1919, i, 215) that hamameli-tannin is an ester-like compound of gallic acid (2 molecules) and a sugar related to the hexoses. The identification of the latter has not yet been accomplished, but it appears to consist of an almost pure aldo-hexose. It does not give the reactions of a pentose. On the other hand, it differs from the usual hexoses in that it cannot be converted into lævulic acid, but its action towards magenta-sulphurous acid and Fehling's solution indicates that it is a true sugar.

Considerable improvements have been effected in experimental

technique. The hydrolysis is effected by tannase (the preparation of which is described in detail), and the process only goes to completion with solutions containing less than 2·5% of the tannin. The course of the action can be followed for the greater part by polarimetric observations or, preferably, by measurement of the gradual increase of the acidity of the solution. The use of lead carbonate and basic lead acetate for the removal of residual gallic acid has been found to be disadvantageous, since the susceptible hamameli-sugar is thereby extensively changed, and these reagents are now replaced by the washed clay of H. Wislicenus, which is found to adsorb gallic acid and tannin from the cold solution without affecting the sugar. An improved method of purifying hamameli-tannin is fully described. H. W.

Physical Properties of some Alkaloids. H. Zeehuisen (*Arch. Exp. Path. Pharm.*, 1920, **86**, 342—372).—Some physical properties, such as odour, solubility, surface tension, electrical charge, according to Zwaardemaker's method, etc., of forty-two alkaloids were studied. The results are tabulated together with some of the properties of these alkaloids previously established.

S. S. Z.

Complex Metallic Ammines. III. Dichlorotetrapyridinecobalt Salts. Thomas Slater Price (T., 1920, **117**, 860—865).

Quinoline-2-, -3-, and -4-sulphonic Acids. E. Besthorn and Bertha Geisselbrecht (*Ber.*, 1920, **53**, [*B*], 1017—1033).—An investigation has been made of the quinoline-2-, -3-, and -4-sulphonic acids which is of particular interest, since quinolines sulphonated in the pyridine nucleus do not appear to have been described previously. In general, the sulphonic acids are well-crystallised substances, the melting points of which are above 270° and have not been determined. They are fairly strong, monobasic acids. The alkali salts are freely soluble in water, as are also the alkaline-earth compounds, although certain of the latter could be obtained in the crystalline condition. The 2-acids are so unstable that they lose sulphur dioxide when their aqueous solutions are boiled, and neither from them nor from the 4-acids was it found possible to prepare the corresponding sulphonyl chlorides or sulphonamides, on account of the readiness with which sulphur dioxide is eliminated. The 3-acids, on the other hand, exhibit a much more normal behaviour.

Quinoline-2-sulphonic acid, slender, colourless needles, is prepared by the oxidation of 2-thiolquinoline with nitric acid (D 1·4) or by the action of boiling aqueous sodium sulphite solution on 2-chloroquinoline. The *silver* salt is described. Similarly, 4-chloroquinoline and sodium sulphite yielded *quinoline-4-sulphonic acid*, colourless needles, the *calcium* salt ($+4H_2O$) and *silver* salt of which were analysed. *4-Methylquinoline-2-sulphonic acid*, obtained by the oxidation of 2-thiol-4-methylquinoline or from sodium sulphite and 2-chloro-4-methylquinoline, forms slender,

colourless needles, which give 2-hydroxy-4-methylquinoline when boiled with water; the *sodium* and *calcium* salts are described. *2-Methylquinoline-4-sulphonic acid* is prepared from 4-thiol-2-methylquinoline or 4-chloro-2-methylquinoline; the *potassium*, *sodium*, *ammonium*, *calcium*, and *silver* salts were investigated.

For the preparation of the 3-sulphonic acids other methods were necessary, since 3-thiolquinoline is unknown, and attempts to prepare 3-thiol-2-methylquinoline from 3-hydroxy-2-methylquinoline were unsuccessful; in addition, the stability of the halogen atom in 3-chloro-2-methylquinoline is such as to render reaction of the substance with sodium sulphite impracticable. The authors have therefore used a method of the Höchst Farbwerke, according to which *o*-aminobenzaldehyde is condensed with sodium acetonesulphonate in aqueous alkaline solution, and have thus obtained 2-methylquinoline-3-sulphonic acid (the *barium* and *silver* salts, the *sulphonyl chloride*, pale yellow needles, m. p. 121°, and the *sulphonamide*, m. p. 227°, are described). Potassium 2-methylquinoline-3-sulphonate is converted by benzaldehyde and zinc chloride at 180° into *2-styrylquinoline-3-sulphonic acid*, which is remarkably stable to acid oxidising agents, but is readily oxidised by potassium permanganate in alkaline solution to a mixture of *2-carboxyquinoline-3-sulphonic acid* and *2-aldehydoquinoline-3-sulphonic acid*, $C_{10}H_7O_4NS,H_2O$ (the *oxime*, colourless needles, and *phenylhydrazone* [?] are described); the aldehyde remains unchanged when boiled with fuming nitric acid or with dilute sulphuric acid and chromic acid, but, on the other hand, a boiling aqueous solution of the *calcium* salt is readily oxidised by silver oxide to the *calcium* salt of 2-carboxyquinoline-3-sulphonic acid, $C_{10}H_5O_5NSCa,4H_2O$ (the *calcium hydrogen* salt is also described). The ready solubility of the free acid in water, combined with the paucity of material, prevented the acid itself from being isolated. The crude acid, however, is converted by concentrated hydrochloric acid at 170° into *quinoline-3-sulphonic acid*, long, colourless, slender needles ($+nH_2O$); the *barium* salt forms colourless, hydrated needles. H. W.

Allyl 2-Phenylquinoline-4-carboxylate. A. Gams (U.S. Pat. 1336952).—*Allyl 2-phenylquinoline-4-carboxylate*, long needles, m. p. 30°, b. p. 260°/15 mm., forms a *hydrochloride*, small, citron-yellow needles, m. p. 145—147°, which is instantly hydrolysed by water. The ester is tasteless, and the hydrochloride has a slight sweet taste. The ester can be made by the usual methods, and has therapeutic properties similar to those of the alkyl esters of 2-phenylquinoline-4-carboxylic acid. Chemical Abstracts.

Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXV. The Binary Systems of Carbazole and Phenols. Robert Kremann and Ferdinand Slovak (*Monatsh.*, 1920, **41**, 23—42. Compare following abstract).—Freezing-point curves have been constructed for the

systems carbazole with α-naphthol, β-naphthol, catechol, resorcinol, quinol, pyrogallol, the three nitrophenols, 2:4-dinitrophenol, and picric acid respectively. It is shown that the two naphthols, pyrogallol, and the three dihydroxybenzenes do not form compounds with carbazole; in all these cases simple eutectics are formed, as follows: α-naphthol, 90·0° with 7% of carbazole; β-naphthol, 115·0° with 9·0% of carbazole; catechol, 102·0° with 4·0% of carbazole; resorcinol, 107·0° with 7·0% of carbazole; quinol, 163·0° with 15% of carbazole; pyrogallol, 126·0° with 1% of carbazole. Similar relationships are found for the nitrophenols and 2:4-dinitrophenol, simple eutectics only being formed, as follows: *o*-nitrophenol, 43·5° with 3·0% of carbazole; *m*-nitrophenol, 92·0° with 5·0% of carbazole; *p*-nitrophenol, 106·7° with 6·0% of carbazole; and *2:4-dinitrophenol*, 98·6° with 17·0% of carbazole. Picric acid forms an equimolecular compound with carbazole, m. p. 183°, and this compound forms an eutectic with carbazole at 181·5° containing 51% of carbazole, and with picric acid at 113° containing 5% of carbazole. J. F. S.

Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXIV. The Binary System Acridine with Phenols. ROBERT KREMANN and FERDINAND SLOVAK (*Monatsh.*, 1920, **41**, 5—21. Compare this vol., i, 570, and preceding abstract).—Freezing-point curves have been constructed for the binary systems of acridine with phenol, α-naphthol, β-naphthol, quinol, catechol, and resorcinol respectively. It is shown that, in the case of phenol and acridine, two compounds are formed, namely, between two molecules of phenol and one molecule of acridine, m. p. 87°, and between two molecules of phenol and three molecules of acridine, m. p. 101°. In the case of β-naphthol, two compounds are also formed, between three molecules of β-naphthol and two molecules of acridine, m. p. 135°, and between one molecule of β-naphthol and two molecules of acridine, m. p. 96°. Acridine and α-naphthol also form two compounds, an equimolecular compound, m. p. 115·5°, and a compound between one molecule of α-naphthol and two molecules of acridine, m. p. 97°. Quinol and resorcinol each form a single compound with acridine of the composition, two molecules of acridine with one molecule of the phenol; these compounds have melting points 209·5° and 179·5° respectively. In the case of catechol, a single compound is also formed, but this is an equimolecular compound, m. p. 144·5°. The affinity of phenol, β-naphthol, and α-naphthol for acridine increases in the order named. J. F. S.

Preparation of *p*-Nitrophenylcarbamide Chloride. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 319969, additional to D.R.-P. 241822; from *Chem. Zentr.*, 1920, ii, 777). —*p*-Nitroaniline is added to a solution of carbonyl chloride in an indifferent solvent, and, if necessary, is further treated with the chloride until the amine hydrochloride has completely disappeared;

temperatures may be employed which are considerably above that at which dry *p*-nitrophenylcarbamide chloride is transformed into the corresponding carbimide. It is preferable first to dissolve the carbonyl chloride, in part or completely, in the solvent, such as nitrobenzene, benzene, or carbon tetrachloride, and then to add the amine. H. W.

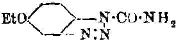
Alteration in Taste of the Sweetening Agent, Dulcin [*p*-Phenetylcarbamide] as a Result of Chemical Change. H. THOMS and K. NETTESHEIM (*Ber. deut. pharm. Ges.*, 1920, **30**, 227—250).—It is found that *p*-phenetylcarbamide,

$$OEt\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2,$$

loses its sweetening power when a considerable variety of acidic or basic substituents is introduced into the benzene nucleus.

The only *p*-phenetylcarbamide substituted in the nucleus which has been described previously is that obtained by Berlinerblau by the action of nitrous fumes on an alcoholic solution of dulcin; this compound is now shown to be 3-nitro-*p*-phenetylcarbamide, since it is identical with the product obtained by the successive action of carbonyl chloride and ammonia on 3-nitro-*p*-phenetidine. (*3-Nitrophenetidine hydrochloride* is obtained as by-product of this action. It commences to dissociate at 130°, and action is complete at 150°. It is extremely readily hydrolysed by water, and the change in colour from the yellow salt to the cinnabar-red base may be conveniently employed in testing for traces of moisture.) 3-Nitro-*p*-phenetylcarbamide may also be obtained by the action of dilute nitric acid on dulcin at the ordinary temperature. (The readiness with which dulcin is converted into its intensely yellow nitro-derivative forms the basis of a convenient and rapid method of distinguishing between dulcin and other sweetening agents.) 2-Nitro-*p*-phenetidine is similarly transformed by carbonyl chloride and ammonia into *2-nitro*-p-*phenetylcarbamide*, long, yellow, shining needles, m. p. 178·5° after softening at 176°. This substance is also obtained by the action of a cold mixture of nitric acid (53%) and concentrated sulphuric acid on dulcin, but the yield is only 60%, as a considerable amount of the latter is destroyed. It cannot be conveniently prepared from 2-nitro-*p*-phenetidine hydrochloride and potassium cyanate in boiling aqueous solution, since the main product of this action is *dinitro*-p-*diphenetylcarbamide*, $CO(NH\cdot C_6H_3[NO_2]\cdot OEt)_2$, yellow needles, m. p. 201°. *3-Nitroso*-p-*phenetylcarbamide* is conveniently prepared by the addition of the requisite quantity of sodium nitrite solution to a suspension of finely powdered dulcin in much concentrated hydrochloric acid; it forms pale yellow needles, which decompose at 51—52°. *3-Amino*-p-*phenetylcarbamide*, needles, decomposing at 179°, is prepared by the reduction of the corresponding nitro-compound with tin and hydrochloric acid; the *hydrochloride*, colourless leaflets, decomposing slowly at 170°, the *sulphate*, prisms, and the *acetyl* derivative, coarse, colourless needles, m. p. 181°, are described. When the salts are treated with nitrous acid, the

diazonium compound is produced, which rapidly passes into the *imino*-derivative (annexed formula), slender needles, m. p. about 141° (decomp.) after softening at 138°. Similarly, 2-nitro-*p*-phenetylcarbamide is reduced by tin and hydrochloric acid to 2-*amino*-p-*phenetylcarbamide*, colourless needles, m. p. 202° (the *hydrochloride* $[+H_2O]$ and *acetyl* derivative, slender, silky needles, m. p. 217—218°, are described).



Nitrous acid converts the substance into a dark brown dye. p-*Phenetylcarbamide-2-sulphonic acid* is prepared by the action of fuming sulphuric acid on dulcin at 50—60°; the sparingly soluble *lead* and the *sodium* salt were analysed. The constitution of the compound is proved by its formation from a boiling aqueous solution of carbamide nitrate and *p*-phenetidine-2-sulphonic acid. It could not be transformed into the corresponding phenol by fusion with potassium hydroxide. 2-*Chloro*-p-*phenetylcarbamide*, small, matted needles, m. p. 148°, is obtained in almost quantitative yield from 2-chloro-*p*-phenetidine hydrochloride and potassium cyanate. The similarly prepared 2-*bromo*-p-*phenetylcarbamide* forms long prisms, m. p. 156°. A *dichloro*-p-*phenetylcarbamide*, needles, m. p. 200°, is obtained from dichloro-*p*-phenetidine by the successive action of carbonyl chloride and ammonia. H. W.

The Sweetening Power of Derivatives of *p*-Hydroxyphenylcarbamide. F. Boedecker and R. Rosenbusch (*Ber. deut. pharm. Ges.*, 1920, **30**, 251—258).—The authors have attempted to obtain a sweetening agent analogous to dulcin (*p*-phenetylcarbamide), but possessing greater sweetening power and greater solubility in water, and have therefore prepared hydroxy-*p*-ethoxyphenylcarbamide, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$, and βγ-dihydroxy-*p*-propoxyphenylcarbamide, $HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$. An improvement in the solubility in water is noticed in either case, but the former compound is less sweet than dulcin and has a bitter after-taste, whilst the latter is not sweet.

Hydroxy-p-*ethoxyphenylcarbamide*, plates, m. p. 160°, is obtained by the action of ethylene chlorohydrin on *p*-hydroxyphenylcarbamide in the presence of sodium ethoxide or, alternatively, by condensing ethylenechlorohydrin with *p*-nitrophenol to p-*nitrophenyl hydroxyethyl ether*, pale yellow needles, m. p. 94—95°, and reducing the latter with zinc dust and hydrochloric acid to p-*aminophenyl hydroxyethyl ether hydrochloride*, needles, m. p. 204—205°, and converting the amino-ether into the corresponding carbamide by an aqueous solution of calcium cyanate. βγ-*Dihydroxy*-p-*propoxyphenylcarbamide*, needles, m. p. 156—157°, is prepared from *p*-hydroxyphenylcarbamide and α-monochlorohydrin.

p-Hydroxyphenylcarbamide reacts with chloroacetamide at 100—110° in the presence of sodium methoxide, yielding p-*carbamidophenoxyacetamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, small leaflets, m. p. 264° after previous softening; it is tasteless.

H. W.

The Iodoamidines. J. Bougault and P. Robin (*Compt. rend.*, 1920, **171**, 38—40).—Benzamidine reacts with iodine in the presence of dilute aqueous sodium hydroxide to give *iodobenzamidine*, m. p. 117°, which is apparently a derivative of hypoiodous acid. It reacts with potassium iodide in the presence of hydrochloric acid, the whole of its iodine being liberated, thus showing that the iodine is linked directly with the nitrogen and is not a substituent of the benzene ring. Anisamidine and piperonamidine give similar crystalline iodoamidines. W. G.

Action of Substituted Hydrazines on the Acyclic αδ-Diketones. E. E. Blaise (*Compt. rend.*, 1920, **171**, 34—36).—Whilst hydrazine gives with acyclic αδ-diketones a mixture of derivatives of pyridazine and tetrahydropyridazine, the substituted hydrazines give pyrrole derivatives. Thus *s*-dipropionylethane gives with phenylhydrazine 1-*anilino*-2:5-*diethylpyrrole*,

$$\begin{matrix}CH{:}CEt \\ | \\ CH{:}CEt\end{matrix}\!\!>N{\cdot}NHPh,$$

m. p. 65·5°. Similarly, with phenylmethylhydrazine, it yields 1-*methylanilino*-2:5-*diethylpyrrole*, b. p. 162°/16 mm., which, when reduced with zinc and hydrochloric acid in acetic acid solution, gives aniline and 2:5-*diethylpyrroline*, b. p. 154°/760 mm. or 62°/28 mm., giving a *platinichloride*, m. p. 180° (decomp.); an *aurichloride*, m. p. 100—101°, and a *picrate*, m. p. 97—98°. Dipropionylethane reacts with ammonia to give 2:5-*diethylpyrrole*, b. p. 100°/29 mm., giving an *oxime*, m. p. 155°. On reduction, the pyrrole gives the 2:5-diethylpyrroline described above. W. G.

Coloured Sensitisers Derived from Quinolines, Quinaldines, and Lepidines containing Dimethylamino- and Diethylamino-groups. H. Barbier (*Bull. Soc. chim.*, 1920, [iv], **27**, 427—439).—6-Dimethylaminoquinoline gives an *ethiodide*, m. p. 212°, and an impure *isomeride*, m. p. 170°, in which the ethyl iodide is probably attached to the nitrogen of the $\cdot NMe_2$ group.

When *p*-phenylenediethyldiamine, glycerol, sulphuric acid, and nitrobenzene are boiled together for three hours, 6-*diethylaminoquinoline*, b. p. 192—193°/20 mm., is obtained, giving a *hydrochloride*, a *platinichloride*, m. p. 280°, a *picrate*, m. p. 196°, a *methiodide*, m. p. 148°, and an *ethiodide*, m. p. 159°.

By the action of paraldehyde on *p*-phenylenedimethyldiamine in hydrochloric acid solution, 6-*dimethylamino*-2-*methylquinoline*, m. p. 101°, b. p. 319°/760 mm., is obtained, yielding a *hydrochloride*, a *sulphate*, a *platinichloride*, m. p. 199° (decomp.), a *mercurichloride*, m. p. 202°, two isomeric *methiodides*, m. p. 230° and 190° respectively, and two *ethiodides*, m. p. 226° and 100° respectively, of which the less fusible compound has the alkyl iodide attached to the ring nitrogen, whilst in the more fusible compound it is united to the alkylamino-nitrogen. Dimethylaminomethylquinoline also gives a *di-ethiodide*.

By the action of a mixture of acetone and formaldehyde saturated with hydrogen chloride on *p*-phenylenedimethyldiamine in hydrochloric acid, 6-*dimethylamino*-4-*methylquinoline*, m. p. 71°,

b. p. 330°, is obtained, giving a *hydrochloride*, a *platinichloride*, m. p. 200°, a *mercurichloride*, m. p. 206°, a *methiodide*, and probably two *ethiodides*.

The alkyl iodides of quinoline, and of 2- and 4-methylquinolines containing a dialkylamino-group, give a series of new colouring matters when condensed either among themselves or with alkyl iodides of other bases. Thus, 6-dimethylaminoquinoline ethiodide yields a cyanine when condensed with 2:6-dimethylquinoline ethiodide. In a similar way, the author has prepared cyanines by condensing the following mixtures: (*b*) 6-Dimethylaminoquinoline ethiodide and 6-dimethylamino-2-methylquinoline ethiodide. (*c*) 6-Diethylaminoquinoline ethiodide and 2:6-dimethylquinoline ethiodide. (*d*) 2:6-Dimethylquinoline ethiodide and 6-dimethylamino-2-methylquinoline ethiodide. (*e*) 6-Dimethylaminoquinoline methiodide and 2:6-dimethylquinoline methiodide. (*f*) 2:6-Dimethylquinoline methiodide and 6-dimethylaminoquinoline amyl-iodide. (*g*) 6-Dimethylaminoquinoline ethiodide and 2:6-dimethylquinoline methiodide. (*h*) 6-Dimethylaminoqninoline methiodide and 2:6-dimethylquinoline ethiodide. (*i*) 6-Dimethylaminoquinoline methiodide and 6-dimethylamino-2-methylquinoline methiodide. (*j*) 6-Dimethylaminoquinoline ethiodide and 4-methylquinoline ethiodide. (*k*) 6-Dimethylaminoquinoline ethiodide and 6-dimethylamino-4-methylquinoline ethiodide. (*l*) 6-Dimethylamino-2-methylquinoline methiodide by itself. (*m*) 6-Dimethylamino-2-methylquinoline ethiodide by itself. (*n*) 6-Dimethylamino-4-methylquinoline by itself. (*o*) Dimethylaminoquinoline ethiodide, 2:6-dimethylquinoline ethiodide and formaldehyde. (*p*) Dimethylaminoquinoline ethiodide, dimethylamino-2-methylquinoline ethiodide and formaldehyde. (*q*) Dimethylamino-2-methylquinoline ethiodide by itself in the presence of formaldehyde. (*r*) *p*-Dimethylaminobenzaldehyde in turn with dimethylamino-2-methylquinoline methiodide and ethiodide, and dimethylamino-4-methylquinoline methiodide and ethiodide.

All these cyanines containing the active auxochrome group, NMe_2 or NEt_2, are of interest in photography as sensitisers.

W. G.

Condensation of 1-Phenyl-3-methyl-5-pyrazolone with Aldehydes and Ketones. S. C. Chatterjee and B. N. Ghosh (*Proc. Asiatic Soc. Bengal*, 1919, **15**, cxxxii—cxxxiii).—When 1-phenyl-3-methyl-5-pyrazolone is heated with aldehydes in molecular proportions, condensation usually takes place with the elimination of water. The compounds thus obtained have the general formula $CHR{:}C{<}\genfrac{}{}{0pt}{}{CO-NPh}{CMe{:}N}$. These substances contain the chromophore ·CO·C:C. and are highly coloured. The present paper describes how aldehydes may be made to unite with pyrazolone, without the elimination of water, to form the intermediate additive hydroxyl compounds, $OH{\cdot}CHR{\cdot}CH{<}\genfrac{}{}{0pt}{}{CO-NPh}{CMe{:}N}$. The chromo-

phoric group, ·CO·C:C, is absent in them, and necessarily they are either colourless, or at any rate much less coloured than the corresponding unsaturated compounds. An attempt to synthesise pyranol derivatives from the pyrazolone and *o*-hydroxy-aldehydes is also described. Some new condensation products with aldehydes and ketones have been prepared, and in this connexion it has been pointed out that the aliphatic ketones are much less reactive than those of the aromatic series. CHEMICAL ABSTRACTS.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXIII. The Binary System Antipyrine–Benzoic Acid. ROBERT KREMANN and HERMANN MARKTL (*Monatsh.*, 1920, **41**, 1—4. Compare A., 1919, i, 458).—Freezing-point curves of the binary mixture benzoic acid and antipyrine have been made, from which it is seen that these two substances form a single equimolecular compound, m. p. 66°; this compound forms an eutectic with benzoic acid at 59·5° containing 50·5% of antipyrine, and one with antipyrine containing 63·5% antipyrine at 59·5° These results show that compounds such as salipyrine are due to combination of the carboxyl group with the antipyrine, and not to the phenolic group, for although phenol does form an equimolecular compound with antipyrine, it is a much weaker compound than that formed in the present experiments.

J. F. S.

Condensation of Benzoin with Diamines. S. C. CHATTERJEE and B. N. GHOSH (*Proc. Asiatic Soc. Bengal*, 1919, **15**, cxxxi—cxxxii).—With the object of preparing substituted naphthadipyridines or pyridinonaphthapyrroles, the reaction between benzoin and some of the naphthylenediamines has been studied, using the corresponding amine hydrochlorides as condensing agents. The reaction took place in the manner desired only in the case of 1:4- and 1:5-diamines, a mol. of the *diamine* combining with 2 mols. of benzoin with the elimination of 4 mols. of water. There are three possible formulæ for each of these substances, and, although no conclusive proof is available, on the strength of indirect evidence it has been suggested that each of the two nitrogen atoms in both these substances forms part of a six-membered ring. Contrary to expectation, the 1:2-diamine yielded a product which appears to be identical with Fischer's diphenyldihydronaphthaquinoxaline (A., 1893, i, 284). Incidentally, the reaction between benzoin and benzidine was also studied, but in this case the closing of the ring did not take place, the compound obtained having the structure $C_{12}H_8(NH{\cdot}CHPh{\cdot}COPh)_2$. An attempt was made to close the ring by boiling with acetic anhydride, but this only resulted in the formation of a diacetyl derivative.

CHEMICAL ABSTRACTS.

The Constitution of Yellow Sulphide Dyes. JATINDRA KUMAR MAZUMDER and EDWIN ROY WATSON (T., 1920, **117**, 830—834).

Decomposition of Nitroso-compounds. II. WILLIAM A. NOYES and JAMES A. COSS (*J. Amer. Chem. Soc.*, 1920, **42**, 1280—1286. Compare Oppé, A., 1913, i, 534).—When an ice-cold alcoholic solution of nitrosophthalimidine is treated with alcoholic sodium hydroxide, *ethyl* o-*diazomethylbenzoate*,

$$N_2\!:\!CH\cdot C_6H_4\cdot CO_2Et,$$

red crystals, m. p. 39°, separate, but at the ordinary temperature after two to three days, or on warming, nitrogen is evolved, and *ethyl phthalaldehydatedihydrazone*,

$$CO_2Et\cdot C_6H_4\cdot CH\!:\!N\cdot N\!:\!CH\cdot C_6H_4\cdot CO_2Et,$$

yellow crystals, m. p. 145°, is produced; this compound is decomposed by hydrochloric acid at 130° into phthalazone and phthalaldehydic acid. *Ethyl* ω-*ethoxy*-o-*toluate*, $CO_2Et\cdot C_6H_4\cdot CH_2\cdot OEt$, an oil, D_{25}^{25} 1·059, n^{25} 1·49556, is produced by boiling an alcoholic solution of the diazo-compound; ω-*ethoxy*-o-*toluic acid*,

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot OEt,$$

melts at 84·5°. Similarly, the product of the action of sodium hydroxide on nitrosoaminolauronic anhydride (Noyes and Taveau, A., 1904, i, 807) is the dihydrazone of camphononic acid, which gives camphononic acid on hydrolysis, accompanied by *ethoxylauronic acid*, $OEt\cdot C_8H_{14}\cdot CO_2Et$, b. p. 113—115°/3 mm. J. K.

The Behaviour of Albumins and Antitoxins towards the Electric Current and the Isolation of Pure Antitoxic Albumin from Diphtheria Serum by the Electro-osmotic Method. W. G. RUPPEL (*Ber. deut. pharm. Ges.*, 1920, **30**, 314—328).—If the blood serum of a normal animal is subjected to the action of an electric current in a cell which is divided into three partitions by suitable semipermeable membranes, and is so arranged that the middle cell contains the serum whilst the outer ones contain pure water in which the electrodes are placed, the fission of the electrolytes and wandering of the ions is first observed, whilst also a number of organic substances, such as amino-acids and degradation products of the albumins, are removed. As soon as the isoelectric point has been reached, the separation of euglobulin commences in the middle cell, and the reaction of the serum passes from neutral or faintly alkaline to acid. After removal of euglobulin, the separation of paraglobulin and albumins can be electrically effected, since the latter are more highly electrically charged, and therefore have a higher velocity of migration. The process can also be applied to the preparation of a pure antitoxic albumin, since it is found that the antitoxins are not in any way damaged or weakened by the electric current. In diphtheria serum, the antitoxin is mainly combined with the paraglobulin, whilst the euglobulin contains only small amounts of antitoxin, and the albumin practically none. The procedure has the advantage over precipitation methods that the usual inactive ingredients of the serum of immunised animals are also removed, whilst the danger of bacterial impurities can easily be avoided. H. W.

Tyrosine and the Dibasic Amino-acids in the Proteins of Yeast. PIERRE THOMAS and ANDRÉ CHABAS (*Compt. rend.*, 1920, **170**, 1622—1625).—An examination of the two proteins, cerevisin and zymocasein, previously found in yeast (compare A., 1913, i, 942, 1026), shows that cerevisin contains 4·13% of tyrosine, 6·26% of glutamic acid, and about 1% of aspartic acid. Zymocasein contains 2·85% of tyrosine, 0·94% of glutamic acid, and about 1% of aspartic acid. In the estimation of glutamic acid, the authors recommend the recrystallisation of its hydrochloride from 96% alcohol, in order to free it from ammonium chloride.

W. G.

Hæmoglobins. J. THONNARD (*Compt. rend. Soc. Biol.*, 1920, **83**, 441—442; *from Chem. Zentr.*, 1920, i, 895).—In the reduction of oxyhæmoglobin with ammonium sulphide for distinguishing it from carbon monoxide hæmoglobin, the concentration of the reducing agent, the temperature, and the origin of the blood are of considerable importance. Experiments with human and animal blood are described. Under similar conditions, the oxyhæmoglobins of warm-blooded animals are much more stable than those of cold-blooded animals. H. W.

Carbon Monoxide Hæmoglobin. J. THONNARD (*Compt. rend. Soc. Biol.*, 1920, **83**, 443—444; from *Chem. Zentr.*, 1920, i, 895).—The times have been measured which, at different temperatures and with a uniform current of gas, are necessary for the conversion of carbon monoxide hæmoglobin by hydrogen into reduced hæmoglobin and by oxygen into oxyhæmoglobin, the experiments being performed with the blood of man, ox, and carp. The results show a complete parallelism between these actions and the stability of oxyhæmoglobin towards ammonium hydrogen sulphide (preceding abstract). H. W.

The Production and Properties of Pathological Melanin. E. SALKOWSKI (*Arch. path. Anat.*, 1920, **227**, 121—137).—Melanin was obtained from the intestinal tract and from tumours. A total of 995 grams of intestine yielded only 0·4406 gram of melanin, or 0·044%. In the preparation of melanin it is necessary to avoid heating with concentrated hydrochloric acid, since this may lead to the formation of melanoidin. The last traces of protein and fat can be removed by heating with glacial acetic acid. By this method, melanin is obtained in two fractions, one soluble in dilute sodium hydroxide, another insoluble even in 15% sodium hydroxide. By keeping, the soluble portion also tends to become insoluble. Melanin contains sulphur, which is firmly bound. It is resistant to oxidising agents, but is completely destroyed by permanganate in alkaline solution and by a mixture of potassium dichromate and sulphuric acid. Melanin consists in large measure of atom complexes belonging to the cyclic and heterocyclic series, but also contains aliphatic molecules.

CHEMICAL ABSTRACTS.

Melanin and the Brown Endogenous Pigments. B. BRAHN and MARTHA SCHMIDTMANN (*Arch. path. Anat.*, 1920, **227**, 137—152).—I. *Melanin.*—Melanin obtained from human tumours showed the following elementary analysis: C 51·92, H 5·21, N 11·03, S 3·42%. Melanoidin from horn contained: C 52·85, H 5·91, N 10·04, S 5·41%. Melanin is believed to be 3:4-dihydroxyphenylcysteine, $C_6H_3(HO)_2 \cdot CH_2 \cdot C(SH)(NH_2) \cdot CO_2H$. II. *Endogenous pigment.*—The endogenous brown pigments are insoluble in ethyl alcohol and ether. The ability of these pigments to be stained with fat stains is due to extraneous material, and not to fatty acids contained within them. The pigment obtained from a heart showing brown atrophy was physically and chemically identical with melanin. III. *Relation of melanin to adrenaline.*—Melanin, like adrenaline, causes vasoconstriction. It does not cause hyperglycemia when injected intravenously. The action of adrenaline on the heart differs from that of melanin.

CHEMICAL ABSTRACTS.

Esterification of α-Amino-acids. H. A. SHONLE and H. H. MITCHELL (*J. Amer. Chem. Soc.*, 1920, **42**, 1265—1277).—The progress of esterification by the process of Osborne and Jones (A., 1910, i, 447) of individual amino-acids, and of mixtures obtained by the acid hydrolysis of casein, vignin, gelatin, and vegetable albumin, has been studied. The method depends on a determination of both the mineral and the unesterified amino-acids by the method of Sörensen (A., 1908, i, 115), and of the mineral acid alone by a Volhard estimation of chloride ion, allowance being also made for acidity due to addition of silver nitrate, when this has been used for purposes of decolorisation. This was, however, best accomplished by means of barium hydroxide and aluminium sulphate, which are preferable to sodium carbonate and potassium alum (Denis, A., 1911, ii, 163), because they can be quantitatively removed. Alanine can be esterified to the extent of 96%, lysine 82%, glutamic acid 85%, and a mixture of amino-acids 90%. Determination of the total amino-acids after prolonged acid hydrolysis shows that a considerable proportion, 36% of those from casein, undergoes esterification during the removal of water from the crude acids preparatory to esterification by repeated evaporation with alcohol. Of the subsequent esterification, most occurred during the first hour, after which it progressed slowly until equilibrium was reached. There is no unesterifiable residue.

J. K.

Mechanism of Enzyme Reaction. EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 137—142).—A theoretical paper in which a number of hypotheses put forward to explain the mechanism of enzyme action are discussed. J. F. S.

The Influence of Hydrogen-ion Concentration on the Inactivation of Pepsin Solutions. JOHN H. NORTHROP (*J. gen. Physiol.*, 1920, **2**, 465—470).—Pepsin in solution at 38° is most

stable at a hydrogen-ion concentration of about P_H 5·0, this point being independent of the anion of the acid used and of the purity of the enzyme solution. Increasing the hydrogen-ion concentration above P_H 5·0 causes a slow increase in the rate of destruction of pepsin, whilst decreasing the hydrogen-ion concentration causes a very rapid increase in the rate of destruction of the enzyme.

The existence of an optimum range of hydrogen-ion concentration for the digestion of proteins by pepsin cannot be explained on the grounds of destruction of the enzyme by either too weak or too strong acid. W. G.

The Effect of the Concentration of Enzyme on the Rate o! Digestion of Proteins by Pepsin. JOHN H. NORTHROP (*J. gen Physiol.*, 1920, **2**, 471—498).—In certain cases, it is found that th rate of digestion of proteins by pepsin is not proportional to th total concentration of the pepsin, and it is suggested that this i due to the enzyme being in equilibrium with another substance which the author, for convenience, calls peptone. This equilibriur is expressed by the law of mass action, according to the equatio K = concentration pepsin × concentration peptone/concentratio pepsin–peptone, it being assumed that only the uncombined pepsi affects the hydrolysis of the protein. This was expressed as differential equation, and was found to agree with experiments results. Pepsin inactivated by alkali enters the equilibrium to th same extent as active pepsin. Where the concentration of pepton is large with respect to that of the pepsin, that of the substrat being relatively constant, the equation simplifies to Schütz's rul $x=K\sqrt{TEA}$, where x=amount of substrate digested, T=tim E=concentration of pepsin, and A=concentration of substrate.

An integral equation, identical with that of Arrhenius for th action of ammonia on ethyl acetate, is obtained, which holds fc the entire course of the digestion, except for the first few minute with varying enzyme concentration.

It is shown that there are many analogies between the action c pepsin on albumin solutions and that of toxins on an organism. W. G.

Properties of a Specially Prepared Enzymic Extrac Polyzime, and comparison of its Starch Liquefying Powe with that of Malt Diastase. JOKICHI TAKAMINE, jun., and KOKICI OSHIMA (*J. Amer. Chem. Soc.*, 1920, **42**, 1261—1265).—Polyzin is an aqueous extract of diastatic enzymes, D 1·03—1·06, containin many other enzymes, made by a specially prepared culture c *Aspergillus oryzae* on media, consisting mainly of wheat bran. I amyloclastic power by Wohlgemuth's method is $D^{40°}_{30\text{ min.}}$ 3·00($D^{40°}_{24\text{ hours}}$ 115·000; whilst Lintner's saccharogenic value at 21° is 4. and at 50°, 150. Its diastatic power remains unchanged at tl ordinary temperature for six months, but is diminished after thr hours above 40°. Its chemical composition is also given. J. K.

Chemical Kinetics of Catalase. II. Catalase from a Germinated Bean: Glycine hispida maxim. EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 59—73. Compare this vol., i, 194).—The enzyme from germinated beans, *Glycine hispida maxim*, was obtained as a dry, very active powder by digesting the crushed beans with distilled water saturated with toluene. The rate of decomposition of hydrogen peroxide by means of the catalase, *G. hispida* has been studied at 0°, 10°, 18°, and 25°, and it is found that the reaction follows the theory previously put forward for the catalase *Phyllostachys mitis*, Riv. (this vol., i, 453). There is a remarkable difference between the two kinds of enzyme. The temperature-coefficient of the rate of decomposition is $\beta_{k'} = 1.40$ for *P. mitis* and 1·85 for *G. hispida*. The difference observed is much too great to be attributed to the effects of the coexisting proteins. To test this point, the reaction was carried out with the enzyme containing different quantities of the coexisting soluble proteins, when no difference was found in the value of k'. It seems probable that catalase is a common name for a group of enzymes which have the power of catalysing hydrogen peroxide. These enzymes have different stabilities by which they may be recognised, and they probably have different physical properties. J. F. S.

Chemical Kinetics of Catalase. III. Effect of Chemical Reagents on the Kinetics of Catalase. EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 75—88. Compare preceding abstract).—The effect of adding small quantities of various substances to the reaction mixture of catalase and hydrogen peroxide has been studied at 0°. The experiments were carried out by adding to 18 c.c. of water 2 c.c. of a mixture of the catalase and the other chemical substance; this is kept at 0° for some time, usually about an hour, and then 4 c.c. of 0·1*N*-hydrogen peroxide is added. The rate of reaction is then measured in the usual way. The reactions are controlled by a similar procedure, but leaving out the foreign substance. The influence of the added substance is calculated from the equations, $r_1 = kE_0/kE_{0\,(control)}$; $r_2 = k'/k'_{(control)}$ in which kE_0 and k' are the initial activity and decomposition constants in the presence of the added substance, and $kE_{0(control)}$ and $k'_{(control)}$ are the same values in the absence of the control; r_1 and r_2 are the coefficients of depressions of the activity. It is found that mercuric chloride, potassium cyanide, hydroxylamine, and phenylhydrazine entirely stop the reaction; strong oxidising agents such as potassium chlorate, potassium nitrate, and potassium dichromate retard the reaction very much; manganese sulphate increases the reaction, as also do soluble starch, glycine, and sucrose; dextrose is entirely without action. All other substances used retard the reaction; the order of the effect, starting with the greatest retardation, is aniline, silver sulphate, ferric alum, acetonitrile, ammonium molybdate, potassium dichromate, copper sulphate, yellow phosphorus (15 c.c. sat. sol.), chrome alum, potassium nitrate, mercuric cyanide, potassium chlorate, alanine, quinine, sodium

carbonate ($N/100$), brucine, sodium oleate, salicin, potassium chloride, asparagine, arsenious acid, menthol (15 c.c. sat. soln.), cobalt sulphate, urethane, ammonium vanadate, ammonium sulphate ($N/1875$), dextrose. The concentration used was $N/1200$, except where the contrary is stated. The effects of the electrolytes are attributed to oxidation, adsorption, or combination with the enzyme, and, as a secondary action, coagulation. J. F. S.

Chemical Kinetics of Catalase. IV. Catalase from the Blood of Cattle. EIICHI YAMASAKI (*Sci. Rep. Tôhoku. Imp. Univ.*, 1920, **9**, 89—95. Compare preceding abstracts).—The reaction between catalase from the blood of cattle and hydrogen peroxide has been examined at 0°, 12·5°, 10°, 18°, and 25°. The reaction is similar in every respect to that observed with catalase from other sources. The temperature-coefficients are $k=1{\cdot}28$ and $k'=1{\cdot}63$, which indicate that the present catalase differs from those previously examined.

Investigations with catalase from various sources show that the decomposition of the enzyme is approximately proportional to that of the hydrogen peroxide. When the enzyme is kept in the solid state for about a year, it is changed into a less active variety. The rate of reaction is expressed by $-dC/dt=kEC$ and

$$(-dE/dt)/(-dC/dt)=k'/k.$$

The course of the reaction may be attributed to the fact that most of the labile kind of catalase had decomposed and that the chief *rôle* was taken by the stable variety. Similar behaviour was also found with solutions of the ferments which had previously been treated with hydrogen peroxide. This may also be attributed to the fact that the labile form decomposes more rapidly with hydrogen peroxide than the stable form. J. F. S.

Action of Poisons on an Enzymatic Process. VI. Comparative Experiments on the Action of Certain Potassium and Sodium Compounds. C. G. SANTESSON (*Skand. Arch. Physiol.*, 1920, **39**, 236—256; from *Chem. Zentr.*, 1920, iii, 18—19).—The influence of a series of potassium and sodium salts on the ability of the catalase of frog's muscle to decompose hydrogen peroxide has been studied. In general, action of a salt depends on the anion rather than the cation. The anions may be approximately arranged in the following order:

$$SO_4,\ PO_4>F>Br>I>CO_3>Cl>BrO_3>ClO_3>NO_3>CN,$$

in which the first member is least and the last most potent. The following series is established for the cations of a number of chlorides: $Mg>Zn>Ba>K>Sr>Ca>Na>Fe$. The order is not invariably maintained with different concentrations. H. W.

Urease. ARNOLD HAHN (*Ber. deut. pharm. Ges.*, 1920, **30**, 329).—In their recent communication, Wester and Pin Yin Yi appear to

have completely overlooked the fact that certain of the results which they describe have been obtained previously by the author.

H. W.

Chemical Kinetics of Urease. EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 97—136).—The decomposition of urea by urease has been investigated under various conditions. The enzyme used was obtained from the soja bean by powdering the beans, extracting the powder with water saturated with toluene, filtering, and precipitating the filtrate with alcohol. The precipitate is washed with absolute alcohol and dried in a vacuum over calcium chloride. It is shown that when the reaction was examined in a faintly acid solution in the presence of a constant stream of carbon dioxide, the reactions $CO(NH_2)_2 \rightarrow NH_2{\cdot}CO_2NH_4 \rightarrow (NH_4)_2CO_3$ take place with about the same velocity. Since the initial velocity $[-dc/dt]_{t=0}$ is unaffected by any factor, the velocity constant k_1 of the first reaction is determined by $[-dC/dt]_{t=0}/C_0 = k_1$, from which it is shown that k_1 is proportional to the concentration of the urease, when the initial concentration of the urea is taken as constant. But it is a somewhat complicated function of the initial concentration of the urea, even though a constant quantity of urease is used at the start; the relationship is $1/k_0(k_0 - k) = 8{\cdot}2C_0^{0{\cdot}8}$, where k_0 is the velocity constant for $C_0 = 0{\cdot}002$; k_0 is taken as the standard because the effect of urea on urease can be reasonably neglected in such a dilute solution. The constant k of the *second reaction seems to be independent of the initial concentration of urea, but it is approximately proportional to that of the urease.* Although the ferment forms an heterogeneous system with the substrate, the reaction is homogeneous, that is, the decomposition of the substrate does not take place in the enzyme phase; at the same time, the rate of hydrolysis is not that with which the substrate diffuses into the enzyme phase, because the reaction is not affected by stirring. The mechanism of the reaction does not consist in the decomposition with a measurable velocity of an intermediate compound formed instantaneously by the reacting components, as is generally accepted. Further, the enzyme and the substrate do not form an intermediate compound with a measurable velocity, and the latter is not decomposed into the products of reaction and the enzyme as is assumed by van Slyke and Cullen. It is a simple catalytic action carried on in the substrate phase. The activity of the catalyst, however, is instantaneously diminished in an irreversible manner by the substrate, according to the equation given above. The experimental results are calculated by means of the formulæ $C_{M_1} = C_0e^{-kt}$; $C_{M_2} = C_0 . k_1/(k_2 - k_1) . (e^{-k_1t} - e^{-k_2t})$; $C_{M_3} = C_0[1 - 1/(k_2 - k_1) . (k_2e^{-k_1t} - k_1e^{-k_2t})]$, and it is found that there is a fair agreement between the calculated and observed values. The temperature-coefficients for k_1 and k_2 are 1·90 and 1·93 respectively. The addition of electrolytes diminishes the activity of the enzyme, due to the adsorption of them by the enzyme. The effects are calculated by Freundlich's formula for hydrochloric acid,

$h=1/k_0 \cdot (k_0-k_1)=107C^{0.5}$; for mercuric chloride, $h=108.3C^{0.3}$; and for silver sulphate, $h=1000C^{0.63}$. The effect of alkalis is reversible, but that of acids is irreversible. Consequently, the Michaelis relationship, $\psi'/\psi=1/(1+[OH]/q)$, is applicable to the alkalis, but $\psi'/\psi=1/(1+q/[H^{\cdot}])$ does not hold for acids, because the action of the hydrogen ion is irreversible. J. F. S.

The Action of Iodine on Arsenious Acid and its Phenyl Derivatives. PAUL FLEURY (*Bull. Soc. chim.*, 1920, [iv], **27**, 490—507).—Iodine reacts with arsenious acid and with the corresponding tervalent phenyl derivatives of arsenic (phenylarsine, diphenylarsine, and triphenylarsine) in the same manner, converting them all into the corresponding arsenic compounds. The action is, however, a balanced one, the hydriodic acid formed tending to reduce the arsenic compounds. In aqueous solution, if their insolubility did not oppose the action, the oxidation of the three phenylarsines would be complete under conditions where arsenious acid would give an equilibrium reaction. Phenylarsine is, however, very sharply distinguished from the di- and tri-phenylarsines, both in the velocity of its oxidation and the equilibrium attained under uniform conditions. The four compounds form a continuous series, in which the oxidisability by iodine increases from arsenious acid up to triphenylarsine. It is of interest to note that both potassium iodide and alcohol, far from diminishing the reducing action of hydriodic acid on the arsenic compounds, rather increase the reduction, and if both iodide and alcohol are present in sufficient concentration, may totally invert the action.

W. G.

Production of Aromatic Arsenic Compounds [Mono- and Di-aryl Arsenious Haloids]. (SIR) WILLIAM JACKSON POPE (Brit. Pat. 142880).—Mono- and di-aryl arsenious haloids are obtained by bringing an arsenious haloid in the liquid or vapour phase into intimate contact with a triarylarsine heated to a high temperature under ordinary atmospheric pressure. According to the proportion of arsenious haloid employed, reactions expressed by the following equations, in the typical case of the phenyl arsenic chlorides, occur: (1) $AsPh_3+2AsCl_3=3AsPhCl_2$;

(2) $2AsPh_3+AsCl_3=3AsPh_2Cl$;

(3) $AsPh_3+AsCl_3=AsPh_2Cl+AsPhCl_2$; (4) $AsPh_2Cl+AsCl_3=2AsPhCl_2$; (5) $AsPhCl_2+AsPh_3=2AsPh_2Cl$. For these reactions with triphenylarsine a temperature approaching 350° is favourable. The products may be separated by any physical or chemical means, or should the diaryl compound be required as the main product, any monoaryl compound present in the reaction mixture may be converted by gently boiling with triphenylarsine, as expressed by reaction (5) above, and, conversely, should the monoaryl compound be required, dry diaryl arsenious chloride present is transformed according to reaction (4). G. F. M.

Preparation of Aromatic Arsinic Acids. ANTOINE MOUNEYRAT (Brit. Pat. 142947).—Aromatic arsinic acids are produced by the interaction of aromatic diazonium compounds with cold or warm aqueous or dilute alcoholic solutions of arsenious acid, in acid, neutral, or alkaline medium in the presence of a copper salt and a reducing agent adapted to the acid or alkaline medium employed. In acid medium, for example, hypophosphorous acid or cuprous hydroxide is suitable, whilst in neutral or alkaline medium, sodium hyposulphite, sodium formaldehyde sulphoxylate, or even an excess of alkaline arsenite may be employed. The method of procedure is capable of numerous modifications in detail, of which examples are given. [See, further, *J. Soc. Chem. Ind.*, 1920, 527A.] G. F. M.

Arsinic Acids Derived from Guaiacol and Veratrole. Constitution of the Polyarsenides. ROBERT GEORGE FARGHER (T., 1920, **117**, 865—875).

A Sulphur Compound which is Present in Very Small Amounts in Salvarsan. C. STRZYZOWSKI (*Korr.-Bl. Schwei. Aerzte*, **47**, 176; *Zentr. Biochem. Biophys.*, 1918, **19**, 794. Compare Fargher and Pyman, T., 1920, **117**, 372).—The author has detected in salvarsan a sulphur compound, which is possibly a sulpho-acid. CHEMICAL ABSTRACTS.

Sodium Compound of Diaminodihydroxyarsenobenzene Dihydrochloride. U. SUZUKI (U.S. Pat. 1330288).—The dihydrochloride is moistened with ethyl alcohol and dissolved in methyl alcohol, and to the solution is added gradually a solution of sodium ethoxide or methoxide until a test portion gives a clear solution in a considerable excess of water. The whole liquid is added to ether containing 6—10% of ethyl alcohol, whereby the desired sodium compound is obtained as a yellowish-brown precipitate, which is washed with ether and dried in a vacuum. The whole process should be carried out in an atmosphere of hydrogen or nitrogen to prevent the possible formation of poisonous or deleterious substances, which may be produced in the presence of even small quantities of oxygen. The product contains 22—25% of arsenic, and its aqueous or physiological sodium chloride solution is suitable for injection. CHEMICAL ABSTRACTS.

Physiological Chemistry.

The Analysis of the Carbon Dioxide Equilibrium in Blood According to H. Straub and K. Meyer. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1920, **103**, 53—59).—A critical discussion of the works of Straub and Meyer (A., 1918, ii, 46

919, i, 53; this vol., i, 200) on the combination of hæmoglobin with carbon dioxide. S. S. Z.

The Catalase of the Erythrocytes. H. VON EULER and E. BORGENSTAM (*Biochem. Zeitsch.*, 1920, **102**, 124—131).—The catalase in the erythrocytes of horse's blood is activated by heat. At 57°, an increase in the activity amounting to 170% was observed. Chloroform and toluene activated the catalase only to a small extent. S. S. Z.

Serum Lipochrome. I. A. A. HIJMANS VAN DER BERGH and P. MULLER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 748—757).—Cow's serum was found to contain only carrotene, and egg-yolk and fowl's serum only xanthophyll. Human serum usually contained both pigments, with a preponderance of carrotene. These are similar observations to those recorded by Palmer (A., 1916, i, 186, 863). The authors do not, however, lend support to the suggestion advanced by the American workers that the lipochrome of cow's serum is present in the form of a complex with protein. Evidence is given that aqueous solutions of carrotene, probably colloidal in nature, may be prepared, from which ether will not extract the pigment directly, but only after the addition of alcohol. Other reagents which affect the colloidal state will also "liberate" the carrotene, so that it may be extracted by shaking with ether. Carrotene in the two forms of solution may show different susceptibilities to destruction by light.
J. C. D.

Hæmolytic Action of some Chlorine Derivatives of Methane, Ethane, and Ethylene. W. PLÖTZ (*Biochem. Zeitsch.*, 1920, **103**, 243—271).—Experiments with a number of chlorine derivatives of methane, ethane, and ethylene show that the hæmolytic activity of these compounds is proportional to their molecular weight and to the number of chlorine atoms. Stalagmometric experiments, on the other hand, have shown that there is no relation between the surface tension of these compounds and their hæmolytic activity. S. S. Z.

A Thermostat with an Electromagnetic Regulator and Electrical Heating Apparatus. G. JOACHIMOGLU (*Biochem. Zeitsch.*, 1920, **103**, 49—53).—A description of an arrangement of apparatus suitable for experiments with isolated mammalian organs. S. S. Z.

Sympathomimetic Amines. I. Amino-derivatives of Naphthalene. A. MADINAVEITIA (*Anal. Fis. Quim.*, 1920, **18**, 66—78).—The compounds described were prepared to ascertain whether the physiological action of bases related to adrenaline persists in compounds containing a naphthalene instead of a benzene nucleus and an amino-group in the side-chain in the β-position to the nucleus. *β-Methoxy-a-naphthylethylmethyl-*

mine, $C_{10}H_7·CH(OMe)·CH_2·NHMe$. The corresponding *β-meth-xy-β-phenylethylmethylamine*, $OMe·CHPh·CH_2·NHMe$, b. p. 05—106° at 22 mm., was also prepared, as it had not been escribed previously. 1-*Aminoacetyl-4-methoxynaphthalene*,

$$NH_2·CH_2·CO·C_{10}H_6·OMe,$$

as m. p. 67°. α-*Aminoacetylnaphthalene*, $NH_2·CH_2·CO·C_{10}H_7$, is escribed. Tests on the physiological action (constriction of blood essels) were carried out with the compounds and with β-phenyl-thylmethylamine used as a standard. The tests proved that a aphthalene compound is forty times more active than a benzene ne; that a methoxy-group does not materially affect the physio-ogical properties; and that a carbonyl group in the side-chain lecreases, but a hydroxyl group in the nucleus increases, the action f the compound on the blood pressure. W. R. S.

Chemistry of Vegetable Physiology and Agriculture.

Decomposition of *dl*-Phenylalanine by Bacillus proteus and Bacillus subtilis. Hajime Amatsu and Midori Tsudji (*Acta Scholae Med. Univ. Imperial Kioto*, 1918, **2**, 447—457).—Each micro-organism (*Bacillus proteus* and *B. subtilis*) was permitted to act in pure culture on a nutrient solution which contained inorganic salts, glycerol, *dl*-phenylalanine, and either a phosphate mixture or lactose plus freshly precipitated uranyl phosphate. Incubation occurred for forty days at 37°. Both bacterial species consumed the *dl*-phenylalanine to a marked degree; that which was recovered after the action of *B. proteus* was dextrorotatory; that which was recovered after the action of *B. subtilis* was optically inactive; apparently *B. proteus* acted asymmetrically, whilst *B. subtilis* attacked both antipodes. Both organisms formed phenyl-lactic acid and phenylethylamine. In the presence of lactose and uranyl phosphate, this amine was formed to a marked degree, but the acid could not be found in the culture. In the presence of a phosphate mixture, the acid was the chief product, and only a very small amount of the amine was formed. *B. proteus* produced *d*-phenyl-lactic acid, whilst *B. subtilis* made *l*-phenyl-lactic acid. Chemical Abstracts.

Formation of Tyrosol from *l*-Tyrosine by Bacteria. Kinsaburo Hirai (*Acta Scholae Med. Univ. Imperial Kioto*, 1918, **2**, 425—432).—A strain of *Bacillus lactis aerogenes*, isolated from the fæces of a breast-fed infant, produced small amounts of tyrosol (*p*-hydroxyphenylethyl alcohol) from *l*-tyrosine during incubation for thirty to thirty-three days at 25° or 37°; none was formed at 15°. The yield was increased by addition of a phosphate mixture to the nutrient solution, which also contained uranyl phosphate

and either dextrose or lactose. Tyrosol was not obtained by the action of *B. lactis aerogenes* on tyramine hydrochloride. Another strain of this organism did not produce tyrosol from *l*-tyrosine.

CHEMICAL ABSTRACTS.

The Chemical Composition of the Tubercle bacillus. A. GORIS (*Compt. rend.*, 1920, **170**, 1525—1527).—Tubercle bacilli when washed free from bouillon, dried at 37°, and extracted with chloroform yielded a substance precipitable from chloroform solution by ether, which the author names *hyalinol*, 7 grams being obtained from 1500 grams of dry bacilli. When saponified by sodium hydroxide, the sodium salts of crotonic and *iso*crotonic acids, and a small amount of a substance having an odour of jasmin and mimosa, are obtained. W. G.

Action of Different Acids on the Growth of Mucor. BETTINGER and DELAVAL (*Bull. Assoc. Chim. Sucr.*, 1920, **37**, 254—261).—The mucor employed for saccharification in distilleries is favourably affected in its vegetative growth by a slight addition of mineral or organic acid to the liquefied cereal mash. The optimum amount of acid varies in a general way inversely with the degree of ionisation, but acetic and succinic acids, which are excretion products, exert a disproportionately great inhibitive action when present in more than the optimum amounts, although their influence is very favourable to growth if this amount is not exceeded. [See also *J. Soc. Chem. Ind.*, 1920, 555A.] J. H. L.

The Yeast Saccharomyces thermantitonum. HANS VON EULER and INGVAR LAURIN (*Biochem. Zeitsch.*, 1920, **102**, 258—268).—A strain of *Saccharomyces thermantitonum* emanating from the Institut für Gärungsgewerbe in Berlin was examined by the authors for its growth, fermentation, and inversion capacities. They found that the limits of temperature characteristic for this species have altered after fifteen years' cultivation in the laboratory on beer wort. A similar observation has been previously made by the authors on a strain of *S. thermantitonum* which came from Jörgensen's laboratory. It is therefore concluded that the yeast, during the years of cultivation in the laboratory, adapted itself to a lower temperature. S. S. Z.

Formation and Significance of Hexosediphosphoric Acid in the Metabolism of Yeast. CARL NEUBERG (*Biochem. Zeitsch.*, 1920, **103**, 320—336. Compare A., 1918, i, 91).—Fresh bottom yeast in the presence of toluene does not utilise inorganic phosphate, whilst the same yeast after drying esterifies the phosphates. The formation of hexosediphosphate, therefore, does not take place under normal conditions of alcoholic fermentation. S. S. Z.

Sulphurous Acid and Yeast Fermentation. ERIK HÄGGLUND (*Biochem. Zeitsch.*, 1920, **103**, 299—306).—0·007*N*-Sulphurous acid completely inhibited the fermentation of 1 gram

of yeast in 25 c.c. of solution. 0·005*N*-Acid did not completely nhibit its activity. The toxic effect of sulphurous acid on yeast ermentation is attributed to the undissociated acid. Sodium ulphite showed an inhibitive action as compared with potassium ulphate. A 0·2*N*-potassium sulphate solution increased the ermentation by about 25%. S. S. Z.

Fermentation of Pyruvic Acid under the Conditions of he Fixation Method. [Fermentation of Pyruvate-Sulphite by Yeast.] Carl Neuberg and Elsa Reinfurth (*Ber.*, 920, **53**, [*B*], 1039—1052).—In consequence of the doubts recently ast by Zerner (this vol., i, 350) on the validity of the authors' heory of the intermediate formation of acetaldehyde and pyruvic cid during the course of alcoholic fermentation, the behaviour of he pyruvic acid–sulphite complex has been further studied. It s found that, *under greatly varied conditions, the complex is at east as readily fermented by yeast as is pyruvic acid itself.* All ypes of yeast and yeast preparations decompose pyruvic acid in he presence of an equivalent or greater amount of soluble ydrogen sulphites. Under suitable conditions of permeability, which appear to be comparable with the osmotic requirements of ugar fermentation, the pyruvic acid–sulphite complex, in spite of ts stability, is more readily fermented than the unstable sugar–ulphite compound. The individual experiments include the ermentation of pyruvic acid in the presence of normal sodium ulphite (1 mol.) by top and bottom yeast, of a molecular mixture f the acid and sulphur dioxide by dry top and bottom yeast, of he pyruvate–sulphite complex by the acetone preparations of ither yeast, and by alcohol–ether yeast, of equivalent amounts of yruvic acid and sodium sulphite by fresh toluolised yeast, and by east juice. The fermentation of calcium pyruvate–sulphite and f pyruvic acid in the presence of more than one molecular roportion of sodium sulphite has also been investigated. H. W.

The Phytochemical Reduction of *o*-Nitrobenzaldehyde. F. F. Nord (*Biochem. Zeitsch.*, 1920, **103**, 315—320).—Yeast educes about 10% of *o*-nitrobenzaldehyde to *o*-nitrobenzyl alcohol. he aldehyde group is therefore reduced phytochemically more asily than the nitro-group. S. S. Z.

The Regulator System: Primary Phosphate-Bicarbonate-Free Carbonic Acid, in place of the System: Primary Phosphate-Secondary Phosphate. W. Windisch nd W. Dietrich (*Biochem. Zeitsch.*, 1920, **102**, 141—150).—See his vol., i, 352.

The Velocity of the Photochemical Decomposition of Carbon Dioxide in Living Cells. Otto Warburg (*Biochem. Zeitsch.*, 1920, **103**, 188—218).—When a cell which has been kept in the dark is exposed to intense light, the velocity of assimilation it shows an initial lag before it becomes constant. This lag is

not observed if the cell is exposed to light of low intensity. Oı submitting the cell to darkness after exposure to intense light, th assimilation gradually ceases. The velocity of assimilation in th cell sinks as the pressure of oxygen increases from one-fiftieth t one atmosphere. The rate of inhibition of the narcotic phenyl urethane on the cell is similar to that of the concentration o narcotics as expressed by Freundlich's adsorption curve, which suggests that it is a surface action. Hydrocyanic acid inhibits th photochemical emission of oxygen from carbon dioxide, but no from the intermediate products of respiration formed in the cell it also inhibits the formation of respiratory carbon dioxide in th cell. Oxygen is split off from nitrates and nitric acid by a suspension of vegetable cells on exposure to light. The kinetics o the photolytic action of the cell in assimilation is discussed.

S. S. Z.

The Presence of Copper in the Vegetable Organism E. FLEURENT and LUCIEN LÉVI (*Bull. Soc. chim.*, 1920, [iv], **27** 440—441).—The authors have extended their work on the presenc of copper in plants (compare A., 1911, ii, 445), and have found i to be present in ten other species and to be situated particularl in the leaves. W. G.

The Presence of Copper in the Vegetable and Anima Organisms. E. FLEURENT and LUCIEN LÉVI (*Bull. Soc. chim.* 1920, [iv], **27**, 441—442. Compare preceding abstract).—Th percentages of copper found in a number of plants, and also i certain animal products, such as milk, meat, and egg-yolk, ar given. W. G.

A Case of Favourable Action of Copper on Vegetation L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, **170** 1542—1545).—Cases are reported where copper sulphate added t water-culture solution exerted a favourable action on the growt of roots and stems of pea and wheat plants during the nine day after germination, and on the root and leaf development of lettuc plants during the thirty-three days after germination. In th first case, 0·2 mg. of anhydrous copper sulphate per litre was use and for the lettuce 0·02 mg. per litre gave the best results.

W. G.

Plasmolysing Action of a Certain Number of Vapour P. GUÉRIN and CH. LORMAND (*Compt. rend.*, 1920, **170** 1598—1601. Compare Mirande, A., 1910, ii, 884).—The plasmo lysis was indicated by the liberation of hydrogen cyanide from th young leaves of cherry laurel or the blackening of the leaves o *Aucuba japonica*. All the alcohols and aldehydes examine exerted a plasmolysing action, as did such substances as *p*-benz quinone, pyridine, and dichlorobenzene. In certain cases in whic Mirande (*loc. cit.*) obtained negative results, the authors ha obtained decidedly positive results. W. G.

Colloid-chemical Researches on Plant Plasma. TETSUTARO TADOKORO (*J. Coll. Agr. Hokkaido Imp. Univ., Sapporo, Japan*, 1919, **8**, 143—182).—I. *Alteration of the colloidal properties of plasma by the addition of neutral salts.*—The press juice obtained by macerating wheat sprouts 5—8 cm. long with quartz sand was treated with increasing concentrations of various chlorides and with various salts of magnesium. After keeping a certain time, the sedimentation was compared with that of an untreated control. The results show, in general, flocculation by $AlCl_3 > BaCl_2 > SrCl_2 > CaCl_2 > MgCl_2$, and deflocculation by $KCl > NH_4Cl > NaCl$. Magnesium salts of 0·01*N*-concentration cause flocculation in the order $I > Cl > NO_3 > SO_4 >$ acetate, but at 0·2*N*, whilst the iodide shows steadily increasing flocculation, the other cations show deflocculations in the following order: $SO_4 > NO_3 >$ acetate $> Cl$. With 0·1*N*-calcium salts, flocculation occurs in the following order: acetate $> I > NO_3 > Cl$. Comparing these results with those of other investigators, it is found that salt concentrations which poison wheat also cause colloidal changes in the press juice. II. *Antagonism and the alteration of the plasma colloids.*—Experiments showing the antagonism between various salts in their action on press juice of wheat sprouts were paralleled by pot-culture experiments showing a corresponding effect of the same mixture on the growth of the wheat plant. The following pairs of salts were used: $NaCl$–$CaCl_2$, KCl–$CaCl_2$, KCl–$MgSO_4$, K_2SO_4–$MgCl_2$, $CaCl_2$–$MgCl_2$, $CaCl_2$–$MgSO_4$. The essential basis of antagonism lies in the maintenance of a certain optimum degree of colloidal dispersion, which the author terms "life-colloidality." For example, sodium chloride tends to deflocculate and calcium chloride tends to flocculate, so that the proper balance between them maintains the optimum dispersion. In like manner, asparagine, glycine, and peptone produce flocculation of press juice in increasing order, whilst sucrose, dextrin, and dextrose produce deflocculation. Therefore, as experiments demonstrate, dextrose is antagonistic to calcium chloride, whereas glycine is antagonistic to potassium chloride. Two other series of experiments show that the same basis of antagonism extends to diffusion through the press juice of *Brassica* leaves, and to the effect of the salts, etc., on the enzymic action of wheat sprout amylase and taka-diastase. CHEMICAL ABSTRACTS.

A Quantitative Study of the Effect of Anions on the Permeability of Plant Cells. ORAN L. RABER (*J. gen. Physiol.*, 1920, **2**, 535—539).—The salts used were all sodium salts, the solutions having $p_H = 7 \pm 0·5$, and their effects on the permeability of *Laminaria agardhii*, Kjellm, were determined. When these salts were used in solutions having the same conductivity, the anions arranged themselves in the order I', Br', CNS', Cl', NO_3', $CH_3·CO_2'$, SO_4'', $C_2H_4O_2(CO_2)_2''$, PO_4''', $C_3H_5O(CO_2)_3'''$ as regards their effect on the permeability, there being thus slight differences from Hofmeister's series. Where the salts were used in equimolecular solutions, the series became CNS', I', Br', NO_3', Cl',

$CH_3\cdot CO_2'$, SO_4'', $C_2H_4O_2(CO_2)_2''$, PO_4''', $C_3H_5O(CO_2)_3''$, the salts apparently forming themselves into two distinct groups. W. G.

The Antagonistic Action of Anions. ORAN L. RABER (*J. gen. Physiol.*, 1920, **2**, 541—544).—Distinct antagonism is shown between the acetate and sulphate anions when used as their sodium salts in their effect on the permeability of *Laminaria*. W. G.

Presence in Melilotus and Asperula odorata of Glucosides yielding Coumarin under the Hydrolysing Action of Emulsin. EM. BOURQUELOT and H. HÉRISSEY (*Compt. rend.*, 1920, **170**, 1545—1550).—Three species of *Melilotus* and *Asperula odorata* were all found to contain a glucoside, which, under the influence of emulsin, gave coumarin. It is probable that the glucoside which yields coumarin varies from one plant species to another. W. G.

The Alkaloid Constituents of Rice Polishings. FRANZ HOFMEISTER [with MASAHIKO TANAKA] (*Biochem. Zeitsch.*, 1920, **103**, 218—225).—The author has isolated from rice an alkaloid substance, *oridine*, which possessed anti-neuritic activity, but on purification, it became inactive. The hydrochloride was prepared as follows: Rice meal was extracted with 80% alcohol. The alcoholic extract was evaporated to a syrup in a vacuum, and made up with hydrochloric acid to a solution containing 3% of the acid. After extraction of impurities with ether, the acid solution was concentrated again to a syrup and made feebly alkaline with sodium carbonate, and precipitated with bismuth–potassium iodide solution. After acidifying the filtrate, the precipitation was repeated, and the precipitate was triturated with silver carbonate and decomposed with hydrochloric acid. The substance was then obtained in crystalline form on drying the filtrate. Doses of 5—10 mg. of the hydrochloride were found to be active. The *aurichloride*, $C_5H_{11}O_2N,HAuCl_4$, formed platelets and flat prisms, m. p. 277°. *Oridine hydrochloride*, $C_5H_{11}O_2N,HCl$, forms colourless prisms, m. p. 240°. The free base was a white, hygroscopic powder, soluble in water. It was found to be isomeric with betaine and valine, and, according to its properties, it is conjectured to be related to the pyridine and piperidine groups. S. S. Z.

The Mosaic Disease of Spinach as Characterised by its Nitrogen Constituents. S. L. JODIDI, S. C. MOULTON, and K. S. lysRKLEY (*J. Amer. Chem. Soc.*, 1920, **42**, 1061—1070).—Previous youL on the nitrogen metabolism of the spinach plant (*J. Agric. Aucuch*, 1918, **15**, 372, 381, 385) had led to the assumption that exerted ation takes place in the diseased plant. With the object quinone, rating this, material from other fields and another year Mirande xamined. It is thus shown that the mosaic disease is obtained dec by a lower total, and also nitric, nitrogen content,

but a higher ammoniacal nitrogen content of the diseased leaf tissue. Further, nitrites are present in diseased but not in healthy leaves. Probably as a result of this, the basic (diamino-) and non-basic (monoamino-) nitrogen content of diseased leaf tissue is less than that of healthy tissue. The proportion of protein nitrogen and protein in healthy leaves is greater than in the roots, but in diseased material there is practically no difference, the actual percentages being greater in the latter case, with the exception that the leaves show a higher protein content in health than in disease. It is therefore concluded that denitrification of leaves, but not of roots, is characteristic of mosaic disease. J. K.

The Unsaturated Alcohol of the Essential Oil of Freshly Fermented Tea Leaves. P. VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 758—761).—The alcohol is Δ^{γ}-hexene-α-ol, identical with that obtained by Walbaum from Japanese oil of peppermint (*A.*, 1918, i, 302). J. C. D.

Action of Gaseous Chlorine and Bromine on Medicinal Plants. DOMENICO LIOTTA (*Arch. Farm. sper. Sci. aff.*, 1919, **28**, 152—160, 161—169).—When treated with chlorine or bromine, the leaves of *Nerium oleander* and of *Digitalis purpurea* completely lose their toxic properties. Experiments made with the leaves of *Prunus laurocerasus* yielded no definite results, but the leaves employed were gathered in November, at which time they are almost devoid of amygdalin.

Similar tests were made with leaves of *Pilocarpus pinnatifolius, Arnica montana, Nicotiana tabacum, Atropa belladonna, Lobelia inflata*, and *Aconitum napellus*. In these cases, the aqueous extracts of the leaves are turbid and difficult to filter, but become limpid and easy to filter after the leaves have been treated with chlorine or bromine. In those cases where the aqueous extract causes death, the aqueous extract of the treated leaves produces the same effect.

With the former group, the halogen apparently produces hydrolysis of the glucoside present, whereas, with the latter, a salt of the alkaloid is probably formed. The action of chlorine or bromine may serve to decide whether the active principle of leaves is glucosidic or alkaloidal in character, and such treatment furnishes a simple means of extracting alkaloids from vegetable or animal substances. T. H. P.

Acidity and Acidimetry of Soils. II. Investigation of Acid Soils by means of the Hydrogen Electrode. HENRY G. KNIGHT (*J. Ind. Eng. Chem.*, 1920, **12**, 457—464. Compare this vol., i, 468).—A hydrogen electrode cell suitable for use in soil investigations is described, as are also the results of experiments on the rate of reactions between normal salt solutions and soils, the rate of reaction in the presence of a base, the change in hydrogen ion concentration with change of amount of base and

with time, and the change in conductivity of soil solutions. [See, further, *J. Soc. Chem. Ind.*, 1920, 523A.] W. P. S.

Relative Absorption by Soil of Sodium Carbonate and Sodium Chloride. Thomas H. Kearney (*Soil Sci.*, 1920, **9**, 267—273).—Observations on plants growing in alkali soils have shown that sodium carbonate is more toxic than sodium chloride, whereas many laboratory experiments on the toxicity of added salts have given the reverse result. Experiments were made to determine whether this difference was due to differences in the amount of absorption of the salts by the soil producing soil solutions of very different concentrations. Solutions of sodium carbonate and sodium chloride of varying concentration were added to sand, and after leaving for twenty-four hours for absorption to become complete, the electrical resistance of the sand was determined by the bridge method. The results obtained showed that 63% of the sodium carbonate was absorbed from solution by the sand, whereas only 23% of the sodium chloride was absorbed. J. H. J.

The Absorbent Power of Soil with Respect to Manganese. P. Nottin (*Compt. rend.*, 1920, **171**, 44—47).—Compost or turf absorbs manganese from solutions of manganous salts to a far greater extent than does ordinary soil. This the author attributes to a difference in the crystallographic state of the calcium carbonate present in the soil. He shows that calcite is not acted on by a 1% solution of manganous chloride, whilst aragonite or ktypeite is dissolved to a very large extent, and an appreciable amount of manganese is thrown out of solution. W. G.

Effect of Calcium Sulphate on the Solubility of Soils. M. M. McCool and C. E. Millar (*J. Agric. Res.*, 1920, **19**, 47—54).—Six soils of different types were treated with a saturated solution of calcium sulphate for twenty-four hours. In one series the soil was then simply drained on a filter, and in another series it was washed with distilled water until the amount of soluble material was reduced to a minimum. In both series, the rate of formation of soluble substances at high and low water content was then determined by the freezing-point method and compared with that for untreated soil. In every case, the treatment was found to have caused a very large increase in the rate of formation of soluble substances. Similar treatment with a $N/10$-solution of calcium phosphate, on the other hand, decreased the rate of formation of soluble substances, and when used with calcium sulphate, decreased its effect.

If the carbon dioxide produced may be taken as a measure of biological activities, the effects described above cannot be ascribed to increase in biological activity, but require some other explanation. W. G.

Organic Chemistry.

The Origin of Petroleum. Formation from Free Fatty Acids or Soaps. Formation from Animal Hydrocarbons. AD. GRÜN and TH. WIRTH (*Ber.*, 1920, **53**, [*B*], 1301—1312).—A modification of Engler's theory of the origin of petroleum from fats has recently been put forward by Pictet and Potok (A., 1919, i, 569), who base their ideas on the experimental results obtained by the distillation of sodium stearate and sodium oleate under diminished pressure, whereby they claim to have isolated hydrocarbons of high molecular weight. The authors have attempted to repeat Pictet and Potok's experiments as far as is possible from the description given in the literature, and have obtained totally different results. Paraffins of high molecular weight are not obtained; the main products are liquid unsaturated hydrocarbons and pentatriacontanone, the latter of which is practically completely decomposed when the distillates are fractionated at the ordinary pressure.

The recent isolation of hydrocarbons by Mastbaum, Tsujimoto, and Chapman in considerable quantity from the liver oils of certain fish may possibly have an important bearing on the origin of petroleum. In favour of this hypothesis, it may be noted that these fish are most closely allied to those of past ages, that the animal hydrocarbons with branched chains contain asymmetric carbon atoms which may account for the optical activity of petroleum, and lastly that the conversion of complex hydrocarbons into naphthenes can be readily explained, since, for example, Chapman has found that spinacene yields a cyclic hydrocarbon when distilled over sodium. H. W.

Pyrogenic Acetylene Condensations. VI. RICHARD MEYER and KURT TAEGER (*Ber.*, 1920, **53**, [*B*], 1261—1265).—Further examination of the mixture of picrates obtained from the fractions of higher boiling point derived from the acetylene tar described previously (A., 1919, i, 72) has shown the presence of fluorene, acenaphthene, anthracene, phenanthrene, pyrene, small quantities of fluoranthene, and a hydrocarbon, $C_{17}H_{10}$, m. p. 186°, which yields a picrate, m. p. 231°. H. W.

Catalytic Oxidation of Alcohols by the Use of Metallic Oxides and of Finely Divided Metals. J. B. SENDERENS (*Ann. chim.*, 1920, [ix], **13**, 266—283).—The oxidation of alcohols under the catalytic influence of various powdered metallic oxides (nickel, copper, vanadium, molybdenum, zinc oxides) gave unsatisfactory results in so far as the production of aldehydes or acids is concerned.

Various metals were tried in the form of turnings or powder as

catalysts for this oxidation, but the only one which gave at all satisfactory results was silver. W. G.

The Phosphatides. ERNEST FOURNEAU (*Bull. Soc. chim. Biol.*, 1920, **2**, 67—87).—A general discussion of these substances. It appears certain that ordinary "lecithin" is a mixture of true lecithin and kephalin. J. C. D.

Density and Coefficient of Expansion of $\beta\beta'$-Dichlorodiethyl Sulphide. JOHN A. WILKINSON and CHRIS WERNLUND (*J. Amer. Chem. Soc.*, 1920, **42**, 1382—1385). The density and coefficient of expansion of dichlorodiethyl sulphide have been determined by the dilatometric method at temperatures between 15° and 90°. The density changes uniformly from 1·2790 at 15° to 1·1996 at 90°, the change being 0·001058 per degree. The coefficient of expansion is also uniform over this temperature range, and amounts to 0·000881 c.c. per degree. J. F. S.

Synthetic Notes [Alkyl Sulphuryl Chlorides. α-Bromophenylacetonitrile. α-Bromo-α-oximinoacetone and $\alpha\alpha$-Dichloro-α-nitrosoethane]. WILHELM STEINKOPF, WALTER MIEG, and JULIUS HEROLD (*Ber.*, 1920, **53**, [*B*], 1144—1148).—The methods of preparation (in part new and in part modifications of older processes) of various substances used by the authors in recent work are described.

n-Propylsulphuryl chloride, $OPr{\cdot}SO_2Cl$, b. p. 70—72°/20 mm. (slight decomp.), was on one occasion obtained by the action of sulphuryl chloride on *n*-propyl alcohol; attempts to repeat the preparation from other specimens of the reagents failed for some unexplained reason. *iso*Propyl and *iso*amyl alcohols are converted by sulphuryl chloride into the corresponding *sulphuryl chlorides* but these cannot be distilled, and gradually decompose when preserved at the ordinary temperature. Ethylene chloro- and bromohydrins are almost quantitatively transformed by sulphuryl chloride into *ω-chloroethylsulphuryl chloride*, $SO_2Cl{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$ b. p. 89—94°/water-pump vacuum, and *ω-bromoethylsulphuryl chloride*, b. p. 100—105°/18 mm., respectively. Hydrogen chloride is evolved when sulphuryl chloride acts on ethyl glycollate, glycol monoacetate, and ethyl or methyl lactate, but the other products decompose when distilled or preserved at the ordinary temperature. Methylsulphuryl bromide could not be obtained from the corresponding chloride and hydrogen bromide, or from sodium methyl sulphate and phosphorus pentabromide, or phosphorus and bromine. Methylsulphuryl chloride and potassium thiocyanate in acetone solution yield methyl thiocyanate, $SO_2Cl{\cdot}OMe + KCNS = MeSCN + SO_2Cl{\cdot}OK$. Phenol is exclusively chlorinated by sulphuryl chloride, yielding *o*-chlorophenol and, possibly, 2 : 4-dichlorophenol. The product obtained from phosphorus pentachloride and potassium phenyl sulphate has b. p. 143—145°/45 mm., and appears to be phenylphosphoryl dichloride, $OPh{\cdot}POCl_2$.

Phenylbromoacetonitrile is obtained as a yellow oil, b. p. 132—134°/12 mm., by the action of bromine vapour on phenylacetonitrile at 105° under the influence of powerful light. Tribromoacetyl bromide, b. p. 88—90°/12 mm., 210—215°/atmospheric pressure, is conveniently prepared from tribromoacetic acid and phosphorus tribromide.

Improved methods are given for the isolation of *a*-bromo-*a*-oximinoacetone, COMe·CBr:N·OH, m. p. 123—125°, and of *aa*-dichloro-*a*-nitrosoethane, $CH_3 \cdot CCl_2 \cdot NO$, b. p. 67—69°. H. W.

The Chloro-derivatives of Methyl Formate and Methyl Carbonate. V. Grignard, G. Rivat, and Ed. Urbain (*Ann. chim.*, 1920, [ix], **13**, 229—265).—A full account of work already published (this vol., i, 138, 139). W. G.

The Successive Stages of the Hydrolysis of Triacetin. Eiichi Yamasaki (*J. Amer. Chem. Soc.*, 1920, **42**, 1455—1468).—It is shown that triacetin conforms to the statement that the hydrolysis of an ester formed by a polyhydric alcohol and a monobasic acid takes place according to the simple rule that each ester radicle has an equal rate of hydrolysis. Thus their rates are simply expressed in the same way as those of the successive reactions $M_1 \longrightarrow M_2 \longrightarrow M_3 \longrightarrow M_4$, which have, respectively, the velocity constants $3k$, $2k$, k. M_1 represents the triacetin, M_2 the two isomeric diacetins, M_3 the two isomeric monoacetins, and M_4 glycerol. Detailed results of the hydrolysis of triacetin in 0·961*N*-hydrochloric acid at 35° are given. W. G.

Chemical Nature of Margosic Acids (Fatty Acids of the Nim or Margosa Oil). Recent Conclusions Drawn from Experimental and Clinical Use of (Metallic) Margosates and Ethyl Margosate. K. K. Chatterjee (*Indian Med. Gaz.*, 1919, **54**, 171—174).—The characteristic acid of this oil belongs to the linolic series, and is named *margosic acid* by the author, who suggests $C_{22}H_{40}O_2$ for its formula. It forms about 23% of the total fatty acid present in nim oil. It is liquid at the ordinary temperature, yellow, and is optically inactive. Its sodium and potassium salts are soluble in water; its lead and barium salts are soluble in ether and light petroleum. The zinc, calcium, bismuth, mercury, and silver salts were also prepared. Ethyl margosate, prepared from the mixed fatty acids in this oil, is a clear, reddish-brown liquid having a fruity odour and a high b. p., and is more readily hydrolysed than potassium margosate. One c.c. of it injected intravenously gives rise to no harmful symptoms (in man). Post-mortem findings in a rabbit killed by injecting this compound showed that death was due to asphyxia. The author has treated several cases of leprosy, syphilis, and skin diseases by injecting the ester, sodium, and potassium salts of this acid with marked success.

Chemical Abstracts.

Bromination of Glutaconic Acid and its Diethyl E
P. E. VERKADE and J. COOPS, jun. (*Rec. trav. chim.*, 1920,
586—593).—By exposing dry powdered glutaconic acid in a
layer to the action of bromine vapour for seventy-two hours
authors have obtained *αβ-dibromoglutaric acid*, m. p. 157°,
out the formation of any hydrogen bromide. This acid,
debrominated by means of zinc and dilute sulphuric acid, gave
glutaconic acid. The authors consider that the αβ-dibromoglu
acid obtained is the *trans*-form.

When ethyl glutaconate was brominated, even with the ut
precautions, there was always some hydrogen bromide for
The ester obtained was not pure, but was in all probability
αβ-dibromoglutarate. When debrominated, the only produ
yielded was glutaconic acid. W.

Relations between the Configuration and the Opt Rotatory Power of some Derivatives of Acids of the Su Group. (MLLE) TH. W. J. VAN MARLE (*Rec. trav. chim.*, 1
39, 549—572).—With the view of seeing whether Hudson's
(A., 1917, i, 318), as to the relationship between the directio
rotation and the configuration of the phenylhydrazides of the m
basic acids of the sugar groups, is applicable to other derivatives of
acids, the author has prepared a number of derivatives desc
below.

d-Gluconic acid gives a hydrazide, m. p. 142°, $[\alpha]_D^{12}$ +30·4
water), $[\alpha]_D^{14}$ +20·9° (in pyridine), yielding a benzylidene deriv
m. p. 157°, $[\alpha]_D^{17}$ +46·6° (in pyridine), and a p-*methoxybenzyli*
derivative, m. p. 185°, $[\alpha]_D^{15}$ +54·0° in pyridine; a *p*-bromoph
hydrazide, m. p. 203°, $[\alpha]_D^{20}$ +3·6° (in water), $[\alpha]_D^{9.5}$ −15·3
pyridine); a p-*tolylhydrazide*, m. p. 204°, $[\alpha]_D^{5}$ +5·0° (in wa
$[\alpha]_D^{24}$ +2·0° (in pyridine); an o-*tolylhydrazide*, m. p. 218°, $[\alpha]_D^{22}$ +
(in water), $[\alpha]_D^{17}$ +5·1° (in pyridine); a m-*tolylhydrazide*, m. p.
$[\alpha]_D^{16}$ +4·5° (in water), $[\alpha]_D^{14}$ +2·7° (in pyridine); an *anilide*, m
171°, $[\alpha]_D^{11}$ +50·6° (in water); a p-*toluidide*, m. p. 181°, $[\alpha]_D^{14}$ +
(in water).

d-Mannonic acid gives a hydrazide, m. p. 161°, $[\alpha]_D^{15}$ −3·0
water), $[\alpha]_D^{14}$ −38·8° (in pyridine), yielding a *benzylidene* deriv
m. p. 194°, $[\alpha]_D^{18}$ −8·0° (in pyridine), and a p-*methoxybenzyl*
derivative, m. p. 191°, $[\alpha]_D^{15}$ −18·8° (in pyridine); a p-*bromoph*
hydrazide, m. p. 225°, $[\alpha]_D^{35}$ −7·3° (in water), $[\alpha]_D^{10}$ −24·9° (in pyrid
a p-*tolylhydrazide*, m. p. 208°, $[\alpha]_D^{16}$ −10·9° (in water), $[\alpha]_D^{14}$ −24·
pyridine); an o-*tolylhydrazide*, m. p. 208°, $[\alpha]_D^{16}$ −8·7° (in w
$[\alpha]_D^{14}$ −28·6° (in pyridine), a m-*tolylhydrazide*, m. p. 214°, $[\alpha]_D^{22}$ −
(in water), $[\alpha]_D^{14}$ −24·7° (in pyridine).

d-Galactonic acid gives a *hydrazide*, m. p. 178°, $[\alpha]_D^{13}$ +40·1
water), $[\alpha]_D^{14}$ +31·1° (in pyridine), yielding a *benzylidene* deriv
m. p. 193°, $[\alpha]_D^{18}$ +63·4° (in pyridine), and a p-*methoxybenzyl*
derivative, m. p. 191°, $[\alpha]_D^{16}$ +67·7° (in pyridine); a p-*bromoph*
hydrazide, m. p. 125°, $[\alpha]_D^{18}$ +2·5° (in water), $[\alpha]_D^{19}$ −30·3° (in pyrid

a p-*tolylhydrazide*, m. p. 212°, $[\alpha]_D^{8}$ $+2\cdot9°$ (in water), $[\alpha]_D^{14}$ $-13\cdot5°$ (in pyridine); an o-*tolylhydrazide*, m. p. 191°, $[\alpha]_D^{12\cdot5}$ $+12\cdot2°$ (in water), $[\alpha]_D^{19}$ $-8\cdot6°$ (in pyridine); a m-*tolylhydrazide*, m. p. 174°, $[\alpha]_D^{13}$ $+0\cdot8°$ (in water), $[\alpha]_D^{14}$ $-15\cdot8°$ (in pyridine); an anilide, m. p. 210°, $[\alpha]_D^{17}$ $+62\cdot6°$ (in water); a p-*toluidide*, m. p. 224°, $[\alpha]_D^{15}$ $+72\cdot9°$ (in water); an o-*toluidide*, m. p. 204°, $[\alpha]_D^{11}$ $+49\cdot9°$ (in water); a m-*toluidide*, m. p. 212°, $[\alpha]_D^{14\cdot5}$ $+63\cdot3°$ (in water).

l-Gulonic acid gives a *hydrazide*, a syrup, $[\alpha]_D^{12}$ $+4\cdot3°$ (in water), yielding a *benzylidene* derivative, m. p. 173°, $[\alpha]_D^{17}$ $-11\cdot2°$ (in pyridine), and a p-*methoxybenzylidene* derivative, m. p. 176—177°, $[\alpha]_D^{14}$ $-2\cdot9°$ (in pyridine), a p-*bromophenylhydrazide*, and a p-*tolylhydrazide*, neither of which could be obtained pure.

l-Idonic acid gives a *hydrazide*, a syrup, $[\alpha]_D^{5}$ $-21\cdot8°$ (in water), yielding a *benzylidene* derivative, m. p. 153°; and a p-*tolylhydrazide*, which was not obtained pure.

*iso*Saccharic acid gives a *hydrazide*, a syrup, $[\alpha]_D^{12}$ $-11\cdot6°$ (in water), yielding a *benzylidene* derivative, m. p. 147°, $[\alpha]_D^{17}$ $-48\cdot2°$ (in pyridine), and a p-*methoxybenzylidene* derivative, m. p. 138°, $[\alpha]_D^{14}$ $-36\cdot2°$ (in pyridine).

l-Arabonic acid gives a hydrazide, m. p. 138°, $[\alpha]_D^{12}$ $+52\cdot6°$ (in water), $[\alpha]_D^{14}$ $+61\cdot8°$ (in pyridine), yielding a *benzylidene* derivative, m. p. 208°, $[\alpha]_D^{17}$ $+81\cdot3°$ (in pyridine), and a p-*methoxybenzylidene* derivative, m. p. 208°, $[\alpha]_D^{17}$ $+81\cdot7°$ (in pyridine): a *p*-*bromophenylhydrazide*, m. p. 204° (decomp.), $[\alpha]_D^{17}$ $+2\cdot4°$ (in water), $[\alpha]_D^{9}$ $-19\cdot0°$ (in pyridine); a p-*tolylhydrazide*, m. p. 216°, $[\alpha]_D^{5}$ $+4\cdot08°$ (in water), $[\alpha]_D^{14}$ $-3\cdot1°$ (in pyridine): an o-*tolylhydrazide*, m. p. 203°, $[\alpha]_D^{18}$ $+26\cdot6°$ (in water), $[\alpha]_D^{14}$ $-1\cdot4°$ (in pyridine); a m-*tolylhydrazide*, m. p. 185° (decomp.), $[\alpha]_D^{5}$ $+4\cdot6°$ (in water), $[\alpha]_D^{14}$ $-5\cdot0°$ (in pyridine); an *anilide*, m. p. 204°, $[\alpha]_D^{20}$ $+68\cdot1°$ (in water); a p-*toluidide*, m. p. 200°, $[\alpha]_D^{17}$ $+68\cdot2°$ (in water); an *o-toluidide*, m. p. 172°, $[\alpha]_D^{11}$ $+56\cdot5°$ (in water), and a m-*toluidide*, m. p. 186°, $[\alpha]_D^{11}$ $+67\cdot7°$ (in water).

d-Ribonic acid gives a *hydrazide*, m. p. 150°, $[\alpha]_D^{12}$ $+27\cdot5°$ (in water), yielding a *benzylidene* derivative, m. p. 138—142°, and a p-*bromophenylhydrazide*, m. p. 169°, $[\alpha]^{18}$ $+3\cdot8°$ (in water), $[\alpha]_D^{10}$ $+14\cdot0°$ (in pyridine).

l-Xylonic acid gives a hydrazide, a syrup, $[\alpha]_D^{15}$ $+34\cdot5°$ (in water), yielding a *benzylidene* derivative, m. p. 153—155°.

d-Lyxonic acid gives a *hydrazide*, m. p. 188°, $[\alpha]_D^{14}$ $-3\cdot6°$ (in water), which yields a *benzylidene* derivative, m. p. 175° (decomp.).

The results indicate that Hudson's law (*loc. cit.*) holds equally for the hydrazides, *p*-bromophenylhydrazides, *o*-, *m*-, and *p*-tolylhydrazides, amides, anilides, and *o*-, *m*-, and *p*-toluidides, the rule being applicable for aqueous solutions, but not for solutions in pyridine. The introduction of a phenyl or tolyl radicle into the amide group results in a considerable rise in the rotatory power. Of the three isomeric toluidides, the para invariably has the greatest rotation and the ortho the least.

Usually the *p*-methoxybenzylidene derivatives had a higher rotatory power than the corresponding benzylidene derivatives.

W. G.

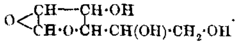
Ring Closure with Polycarboxylic Acids. I. The Dianhydride of Ethanetetracarboxylic Acid. ERNST PHILIPPI and JULIE HANUSCH (*Ber.*, 1920, **53**, [*B*], 1300—1301).—*Ethanetetracarboxylic anhydride*, $O<\begin{matrix}CO\cdot CH\cdot CO\\ CO\cdot CH\cdot CO\end{matrix}>O$, colourless needles, which become discoloured at about 150° and decompose without melting at a higher temperature, is prepared by the action of warm acetic anhydride on ethanetetracarboxylic acid; the latter substance is re-formed by the action of water on the anhydride.

H. W.

Improved Catalyst for the Manufacture of Acetaldehyde from Acetylene as the Primary Material, and Process for the Regeneration of the Catalyst. SOCIÉTÉ DES ACIERIES ET FORGES DE FIRMINY (Brit. Pat. 124194).—An improved catalyst for the hydration of acetylene consists of a solution of sulphuric acid containing mercury, ferric, and vanadium salts, which, after becoming exhausted, can be regenerated by electrolytic oxidation either intermittently or continuously, using a cell with a magnetite or platinum anode and a current density of 3—5 amperes per sq. dcm., the temperature being maintained at 30—40°. By way of example, the catalyst may consist of 10—20% sulphuric acid containing in solution 2% of mercury, 0·3—0·5% of iron, and 0·025—0·1% of vanadium, the metals being present as sulphates. The optimum temperature of the bath for the conversion of acetylene into acetaldehyde is about 65°. G. F. M.

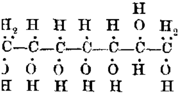
The Alleged Inactivation of *d*-Mannitol. MASTA EHRLICH (*Biochem. Zeitsch.*, 1920, **103**, 312—315).—The author confirms Grün's observation that by dissolving the alkaline earth salts in a mannitol solution, a product is obtained which shows no rotation. Unlike Grün, however, she finds that when the strontium nitrate–mannitol solution is precipitated with acetone, as described by Grün, the mannitol thus obtained is identical with the active mannitol originally used. The mannitol is therefore not inactivated by this treatment, as is alleged by Grün. S. S. Z.

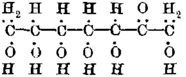
Glucosan. AMÉ PICTET and PIERRE CASTAN (*Compt. rend.*, 1920, **171**, 243—245).—Gélis obtained a brown, amorphous substance, which he named glucosan, by heating dextrose at 170° (compare *ibid.*, 1860, **51**, 331). This compound can be obtained in a pure, crystalline state if the dextrose is heated at 150—155° under a pressure of 15 mm. So obtained, it has m. p. 108—109°, is very deliquescent, and has $[\alpha]_D +69\cdot8°$ in water. It reduces Fehling's solution, and when boiled with water gives dextrose again. When dissolved in methyl alcohol saturated with ammonia, it gives a crystalline *compound*, which is not glucosamine or *iso*glucosamine. When dissolved in methyl alcohol saturated with hydrogen chloride it gives α-methyl glucoside. It yields a *tribenzoyl* derivative and a crystalline *bisulphite compound*. When dissolved in methyl alcohol and mixed with a solution of sodium methoxide in the same solvent, it gives a white *sodium* derivative, which, when

decomposed by dilute sulphuric acid, ultimately gives a methyl glucose. From its general behaviour the authors assign to glucosan the constitution .

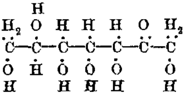
W. G.

Sedoheptose, a New Sugar from Sedum Spectabile. II. F. B. La Forge (*J. Biol. Chem.*, 1920, **42**, 367—374. Compare A., 1917, i, 444).—*a*-Sedoheptitol on oxidation with nitric acid gives pentahydroxypimelic acid. Of the ten theoretically possible heptitols, six are optically active, and of these six, five are known. *a*-Sedoheptitol does not correspond with any of these five, and its constitution must therefore be given by the annexed formula. In the same way, considering the properties of inactive *β*-sedoheptitol and the constitution of the four possible inactive heptitols, of which only one is known, and since the *a*- and *β*-sedoheptitols differ only in having the position of one hydroxyl group reversed, there are only two possible *configurations for an a-ketoheptose which will give such*





(I.)



(II.)

heptitols, namely, formulæ I and II. At present it is not possible to distinguish between these two formulæ. W. G.

Volemitol. F. B. La Forge (*J. Biol. Chem.*, 1920, **42**, 375—376).—*a*-Sedoheptitol gives an acetal, m. p. 191—194°, which is identical with that from the natural heptitol, volemitol, and it is now shown that these two heptitols are identical. The m. p. for *tribenzylidenevolemitol* given by Bougault and Allard (A., 1903, i, 62) is erroneous. W. G.

Optical Properties of a Series of Heptitols. Edgar T. Wherry (*J. Biol. Chem.*, 1920, **42**, 377—382).—The following are the refractive indices and densities of the eight known heptitols:

	n_a.	$n_β$.	$n_γ$.	D.
a-Mannoheptitol	1·538	1·545	1·549	1·485
β-Mannoheptitol	1·533	?	1·545	1·470
a-Glucoheptitol	1·548	1·550	1·558	1·520
β-Glucoheptitol	1·542	1·550	1·552	1·510
a-Sedoheptitol	1·550	1·555	1·562	1·520
β-Sedoheptitol	1·564	1·570	1·584	1·590
a-Guloheptitol	1·554	1·560	1·570	1·560
β-Guloheptitol	1·565	1·570	1·580	1·585

W. G.

The Acidic and Basic Properties of Different Compounds. H. I. WATERMAN and J. GROOT (*Rec. trav. chim.*, 1920, **39**, 573—577).—In continuation of previous work (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, January), it is shown that the three cresols and *o*- and *m*-cresotic acids do not influence the hydrolysis of sucrose by hydrochloric acid, but that they all considerably retard the decomposition of dextrose by dilute aqueous sodium hydroxide. W. G.

Physicochemical Investigations of the Diastatic Inversion of Sucrose. ANDRÉE CHAUDUN (*Ann. chim.*, 1920, [ix], **13**, 301—349).—A more detailed account of work already published (compare A., 1918, i, 414; ii, 357; 1919, ii, 327; this vol., ii, 24). W. G.

Humic Acid. F. FUCHS (*Chem. Zeit.*, 1920, **44**, 551).—Humic acid prepared from peat by the action of alkalis was found to be a true acid, and not a colloidal substance. It formed only simple salts, had a molecular weight of about 680, and contained 57·4% C, 4·6% H, and less than 1% of N and S. The salts of calcium, barium, magnesium, aluminium, copper, and iron were prepared. The silver salt was of variable composition (5 to 50% of silver). The humic acid was precipitated by both inorganic and organic acids. As stated by Albert (A., 1909, ii, 446), it dissolved as lithium humate when treated with lithium phosphate, which was decomposed in the reaction into the monohydrogen phosphate and hydroxide. Alkali humates are precipitated by sodium chloride solution, with the exception of a small residue, which can only be precipitated by acids, and when dried is soluble in sodium carbonate solution, whereas the portion precipitated by sodium chloride is much darker in colour, and when dried does not dissolve in sodium carbonate solution. On treating humic acid with sodium sulphide or sulphite, it yields a soluble sulphite compound, which reacts with aniline and other organic bases. C. A. M.

New Derivatives of $\beta\gamma$-Dibromo-α-aminopropane and a New Base, C_3H_3N. EMIL ABDERHALDEN and MAX PAQUIN (*Ber.*, 1920, **53**, [*B*], 1125—1143).—A series of products is described which originates in the spontaneous decomposition of solutions of $\beta\gamma$-dibromo-α-aminopropane in ether. In general, the constitution of the substances has not been elucidated definitely, but a preliminary account is now given.

When a solution of $\beta\gamma$-dibromo-α-aminopropane in dry ether is allowed to remain at slightly elevated temperature for two to four days, well-defined, prismatic crystals of the substance, $C_3H_3NBr_2,HBr$, m. p. 164°, separate. The success of the experiment depends largely on the dryness of the ether, since the presence of traces of moisture causes the separation of a yellow, amorphous substance (see later), which is only separated with great difficulty from the hydrobromide. The latter is obtained in a purer condition, m. p. 170°, from the hydrobromide of the base,

$C_6H_6NBr_2$ (see later), and is probably identical with the compound obtained in a similar manner by Paal from β-bromoallylamine. The free *base*, $C_3H_3NBr_2$, could not be isolated in the pure condition, since it is not volatile without decomposition, but the following salts are described: *nitrate*, pearly leaflets, m. p. 76° (incipient decomp.); *sulphate*, $(C_3H_3NBr_2)_2H_2SO_4$, crystalline powder, m. p. 195° (incipient decomp.); *formate*, pearly leaflets, m. p. 105° (slight decomp.); *oxalate*, $C_3H_3NBr_2,H_2C_2O_4$, m. p. 173° (decomp.); *picrate*, yellow needles, m. p. 169° (slight decomp.). The base appears to be a secondary amine; it does not give the carbylamine reaction or yield a precipitate with metaphosphoric acid. It gives a *benzoyl* derivative, m. p. 130°, a *benzenesulphonyl* compound, m. p. 85°, a *monomethyl* derivative [*hydrobromide*, slender needles, m. p. 188° (decomp.)], and a *compound*, $C_{10}H_7NBr_2S_4$, m. p. 161° (incipient decomp.), with carbon disulphide. The constitution $HC\lessgtr^{CBr}_{NH}\gtrdot CHBr$ is suggested for the base. It readily reacts with hydrogen in alcoholic solution in the presence of colloidal palladium, yielding the pure hydrobromide, $C_3H_3NBr_2.HBr$, but the fate of the remainder of the molecule could not be established.

The yellow, amorphous substance, $(C_3H_3NBr)_2$ (see above), darkens at about 175° and slowly melts and decomposes between 250° and 260°; it is readily oxidised by bromine, without, however, yielding a product which is itself isolable in the pure state or yields pure salts.

An ethereal solution of the base, $C_3H_3NBr_2$, loses bromine when treated with sodium, and yields the *base*, C_3H_3N, which cannot be distilled without decomposition. Its salts with inorganic acids are extremely hygroscopic, whilst the compounds with organic acids are not generally well defined. It yields, however, an *oxalate*, $C_3H_3N,H_2C_2O_4$, m. p. 127°, a picrate, needles, m. p. 141° (incipient decomp.), and a *compound* with mandelic acid, $C_{10}H_7O_3N$, m. p. 124°. Its close relationship to the parent base is proved by the conversion of its oxalate by bromine into the oxalate,

$$C_3H_3NBr_2,H_2C_2O_4.$$

The constitution of the base is somewhat uncertain, since it does not give the reactions characteristic of secondary or tertiary amines, but the formula $CH\lessgtr^{CH}_{N}\gtrdot CH$ appears most probable. Although highly unsaturated, neither the base itself nor its salts can be hydrogenated in the presence of platinum or palladium under widely varied conditions.

Dehalogenation of the hydrobromide of the base, $C_3H_3NBr_2$, can be partly effected with alcoholic sodium ethoxide or with silver nitrate and nitric acid, but in this case a monobromo-derivative remains, which has not been further investigated.

When ethereal solutions of dibromoaminopropane are allowed to remain in the presence of acetone, the *substances*

$$C_3H_2{:}C_3H_3NBr_2,HBr,$$

m. p. 198° (decomp.), and $C_9H_8NBr_2,HBr$, m. p. 168° (decom are obtained. The former is reconverted into the hydrobrom $C_8H_3NBr_2,HBr$, when the ethereal solution of the liberated base treated with bromine or simply preserved, or when the aque solution of the salt is acted on by excess of bromine. T *formate*, $C_3H_2:C_3H_3NBr_2,H\cdot CO_2H$, has m. p. 167° (decomp.). T hydrobromide of the base, $C_9H_8NBr_2$, can be converted into *oxalate*, $C_9H_8NBr_2,H_2C_2O_4$, m. p. 116° (decomp.), and a *nitra* m. p. 105° (incipient decomp.). The hydrobromide cannot be c verted by oxidative degradation into the substance, $C_8H_3NBr_2,H$ nor can it be obtained from the latter or from $C_6H_5NBr_2,HBr$ the action of acetone. An ethereal solution of the free b deposits crystals of the hydrobromide in the course of a few da The base may be dehalogenated by the action of sodium on ethereal solution, but the corresponding bromine-free compou is decomposed with extraordinary readiness on exposure to air; gives characteristic *compounds* with mercuric chloride, decomposi without melting at 100°, with picric acid, darkening at 150°, b not melting below 250°, and with salicylic acid, not melti below 350°. H. W.

Optically Active Iridium Compounds. A. WERNER a AL. P. SMIRNOFF (*Helv. Chim. Acta*, 1920, **3**, 472—486).—T authors have prepared compounds belonging to two new comp iridium series, and have succeeded in resolving them into th optically active components, confirmation being obtained Delépine's proof that co-ordinated saturated iridium comple possess an octahedral spacial configuration (A., 1914, i, 1048). T action of ethylenediamine on hexahalogenated compounds quadrivalent iridium yields only dark, uncrystallisable syrups, b from ethylenediamine and complexes containing either seve nitro-groups or ammonia united to a tervalent iridium atom, co plexes containing two or three molecules of the diamine are read obtained. The salts thus prepared belong to the dinitrodiethyle diamineiridium and the triethylenediamineiridium series, and colourless and highly stable, those of the former series being solu only slightly, and those of the latter about ten times as solut The nitro-groups of the first series are so firmly united to t metallic atom that it is necessary to heat the compounds for so hours with concentrated sulphuric acid before nitrous acid is sp off; with concentrated sulphuric acid and diphenylamine, the sa of this series give, not the ordinary blue, but a bright red, col ation, which is produced by the sulphuric acid alone. The n series closely resemble, and give the same precipitation reacti as, the dinitrotetrammineiridium series (compare Werner a de Vries, A., 1909, ii, 151) and the hexammineiridium series (co pare Palmaer, A., 1896, ii, 179). Although two dinitro-series possible theoretically, only one has been obtained, and as t α-camphorsulphonates are separable into their optically act components, the compounds are of the *cis*- or 1:2-dinitrodiethyle

diamineiridium series; this separation is readily effected with the help of nitrocamphor. The rotatory power of the triethylenediamine series is greater than that of the dinitro-series, and of about the same order of magnitude as those of the analogous rhodium and platinum compounds (compare Werner, A., 1912, i, 418). In the visible part of the spectrum both series exhibit normal rotatory dispersion.

The two series of compounds were prepared by the action of ethylenediamine monohydrate on sodium dichlorotetranitroiridate in a sealed tube at 170°, and were separated as iodides.

Salts of the racemic dinitrodiethylenediamineiridium series, $1:2\text{-}[(NO_2)_2Ir\,en_2]X$, the *iodide*, *bromide*, *nitrate*, *perchlorate*, and d-(*a-bromo*)-*π-camphorsulphonate*, $1:2\text{-}[(NO_2)_2Ir\,en_2]d\text{-}C_{10}H_{14}O_4BrS$, were prepared.

Salts of the *d*-dinitrodiethylenediamineiridium series: d-*camphorsulphonate*, $d\text{-}[(NO_2)_2Ir\,en_2],d\text{-}C_{10}H_{15}O_4S$; *bromide*, colourless, shining polyhedra, $[a]_C + 17{\cdot}2°$, $[a]_D + 26°$, $[a]_E + 40°$; *perchlorate*, white, crystalline powder, $[a]_C + 16{\cdot}4°$, $[a]_D + 24{\cdot}8°$, $[a]_E + 38{\cdot}4°$; *nitrate*, flat, shining needles, $[a]_C + 18°$, $[a]_D + 27{\cdot}2°$, $[a]_E + 41{\cdot}2°$.

Salts of the *l*-dinitrodiethylenediamineiridium series: l-*camphorsulphonate*, $l\text{-}[(NO_2)_2Ir\,en_2],l\text{-}C_{10}H_{15}O_4S$; *bromide*, $[a]_C - 17{\cdot}6°$, $[a]_D - 26°$, $[a]_E - 40°$; *perchlorate*, $[a]_C - 16{\cdot}8°$, $[a]_D - 25{\cdot}6°$, $[a]_E - 39{\cdot}2°$; *nitrate*, $[a]_C - 17{\cdot}6°$, $[a]_D - 26{\cdot}8°$, $[a]_E - 41{\cdot}6°$.

Salts of the racemic triethylenediamineiridium series, $[Ir\,en_3]X_3$: *bromide* ($+ 3H_2O$), *nitrate*, and *perchlorate*.

Salts of the *d*-triethylenediamineiridium series: *iodide*, $[a]_C + 30°$, $[a]_D + 42°$, $[a]_E + 56°$; *nitrate*, $[a]_C + 41{\cdot}2°$, $[a]_D + 57{\cdot}2°$, $[a]_E + 75{\cdot}2°$; *perchlorate*, $[a]_C + 34{\cdot}5°$, $[a]_D + 48{\cdot}5°$, $[a]_E + 64°$.

Salts of the *l*-triethylenediamineiridium series: d-*camphornitronate*, $l\text{-}[Ir\,en_3](d\text{-}C_{10}H_{15}O_3N)_3$; *bromide*, ($+ 2H_2O$), $[a]_C - 36°$, $[a]_D - 50°$, $[a]_E - 66{\cdot}5°$; *nitrate*, $[a]_C - 41{\cdot}5°$, $[a]_D - 57{\cdot}5°$, $[a]_E - 76°$; *perchlorate*, $[a]_C - 34°$, $[a]_D - 47{\cdot}5°$, $[a]_E - 63°$. T. H. P.

Attempts to Prepare Derivatives of Diaminoacetylene. PAUL RUGGLI (*Helv. Chim. Acta*, 1920, **3**, 559—572. Compare A., 1917, i, 22).—With the object of obtaining derivatives of diaminoacetylene, those methods of decomposition which usually yield amines with one carbon atom less than the original compounds have been applied to acetylenedicarboxylic, dibromomaleic, and dibromofumaric acids. The only method giving promising results is that in which the hydrazide and azide form intermediate steps; with dibromomaleic acid hydrazine forms a closed ring hydrazide, with dibromofumaric acid degradation occurs in the desired direction, but has not as yet been carried sufficiently far. Unlike iminazole itself, tribromoiminazole yields no ethylene derivative, but merely a benzoyl compound when treated with benzoyl chloride.

Details are given for obtaining large quantities of bromine-free acetylenedicarboxylic acid by Bandrowski's method (this Journ., 1877, ii, 592; compare Michael, A., 1893, i, 144; von Baeyer, A., 1885, 759, 1198).

Treatment of dibromomaleic acid in pyridine solution with zinc dust yields, in the hot, resinified products, and in the cold only the *pyridine* salt of the acid, $C_4H_2O_4Br_2,C_5NH_5$, m. p. 120° (decomp.); no indications of the existence of a normal salt were obtained.

Ethyl acetylenedicarboxylate, prepared by esterification of the acid, forms crystals, m. p. 1—2°, D_4^{15} (liquid) 1·0690. When prepared by reducing ethyl dibromomaleate with zinc dust, the ester is accompanied by a considerable proportion of resinous matter which cannot be distilled (compare Michael, *loc. cit.*).

The action of hydroxylamine on ethyl acetylenedicarboxylate in presence of sodium ethoxide yields the crystalline, hygroscopic *sodium* salt, NOH:C(ONa)·C:C·CO_2Na, or possibly

$CO_2Na·C(NH·OH):CH·CO_2Na \rightleftharpoons CO_2Na·C(:NOH)·CH_2·CO_2Na$,

which forms an alkaline, aqueous solution, decolorises permanganate instantaneously, explodes slightly when heated, and with ferric chloride gives the deep violet coloration or precipitate characteristic for hydroxamic acids. Benzoylation by the Schotten-Baumann method gave small proportions of a crystalline compound, which was not examined further. When liberated by the action of dilute acid, the hydroxamic acid itself undergoes decomposition.

Chlorofumaric chloride, COCl·CCl:CH·COCl (compare Perkin, T., 1888, **53**, 696; Ruggli and Hartmann, this vol., i, 636), prepared by the action of phosphorus pentachloride on acetylenedicarboxylic acid, has b. p. 73—75°/20 mm.

Dibromofumaric dihydrazide,

$NH_2·NH·CO·CBr:CBr·CO·NH·NH_2$,

prepared from dibromofumaric chloride and hydrazine hydrate forms crystals decomposing at about 154°. In this preparation most of the material is converted into a brown powder, which carbonises at a high temperature.

Dibromofumaric diazide, N_3·CO·CBr:CBr·CO·N_3, obtained by treating the dihydrazide with nitrous acid, forms a white powder and in the dry state explodes violently when gently rubbed. When heated with alcohol it yields nitrogen and a crystalline compound which is evidently diamidodibromoethylene carbamate, and is to be investigated.

2:4:5-*Tribromo*-1-*benzoylglyoxaline*, $NBz<\begin{matrix}CBr:N\\ CBr:CBr\end{matrix}$, forms stout crystals, m. p. 101—102°. T. H. P.

Dipeptide of Aspartic Acid and Function of Asparagine in Plants. C. Ravenna and G. Bosinelli (*Gazzetta*, 1920, **50**, i, 281—288; *Atti R. Accad. Lincei*, 1920, [v], **29**, i, 278—282).—When boiled, aqueous solutions of asparagine yield the dipeptide of aspartic acid, together with a little aspartic acid. Neither the latter nor its ammonium salts give the dipeptide under similar conditions (compare this vol., i, 150, 151, 373). The fundamental function of asparagine and of amides of amino-acids generally in plants appears to be to render possible the synthesis of polypeptide

and hence that of proteins; the results of the experiments with aspartic acid indicate that direct formation of proteins from the simple amino-acids does not occur.

Since the dipeptide obtained by the authors is formed only from asparagine, *to which Piutti ascribes the structure of β-asparagine* (A., 1889, 383), its structure is probably

$$CO_2H{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

whereas Fischer and Koenigs' dipeptide (A., 1907, i, 486) is probably the α-isomeride of the formula,

$$CO_2H{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}CO{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2H.$$

T. H. P.

Trichloroacetimino-methyl and -ethyl Ethers. WILHELM STEINKOPF and RUDOLF SEMMIG (*Ber.*, 1920, **53**, [*B*], 1149—1152).—The conversion of nitriles into imino-ethers has been supposed by Houben (A., 1913, i, 958) to occur in accordance with the scheme $R{\cdot}CN + HCl \longrightarrow R{\cdot}CCl{:}NH \xrightarrow{MeOH} R{\cdot}C(OMe){:}NH + HCl$. Although generally agreeing with this view, the authors do not consider it applicable to the special case of trichloroacetonitrile, which is converted by methyl alcohol in the absence of hydrogen chloride into trichloroacetiminomethyl ether and in the presence of the acid into trichloroacetamide (compare Steinkopf, A., 1907, i, 488). Further examination of the action shows that catalytic influences play a most important part, and, of these, the presence of trichloroacetamide in the nitrile and of acetone in the methyl alcohol appears to be the most important; with pure materials, the presence of hydrogen chloride greatly diminishes the rate of reaction. Similarly, pure ethyl alcohol does not react with nitrile containing amide, but action may be caused to occur both with pure and contaminated nitrile if a few drops of acetone are added. *Trichloroacetiminoethyl ether*, $CCl_3{\cdot}C(OEt){:}NH$, is a highly unstable substance, b. p. 74—79°/35 mm., which could not be isolated in the pure state. H. W.

Mercuric Oxycyanide. A. J. JONES (*Pharm. J.*, 1920, **105**, 87—89).—This compound may be prepared by grinding together 40 grams of mercuric cyanide, 30 grams of yellow mercuric oxide, and 15 c.c. of water for fifteen minutes; 0·5 c.c. of 20% sodium hydroxide is then added, and the stirring continued with the addition of further small quantities of water. After about eighteen hours the mass is diluted with 200 c.c. of water, rendered slightly acid with acetic acid, using phenolphthalein as indicator, and added to 700 c.c. of boiling water containing 20 grams of mercuric cyanide. The mixture is boiled until solution is almost complete, filtered, and cooled. The crystals are collected, washed with a small quantity of cold water, and dried over sulphuric acid. With more concentrated solutions than mentioned above, separated crystals of the oxycyanide are liable to decompose, and explosion has occurred during the preparation of the compound. W. P. S.

The Preparation of Trimethylarsine and Trimethylarsine Selenide. R. R. Renshaw and G. E. Holm (*J. Amer. Chem. Soc.*, 1920, **42**, 1468—1471).—For the preparation of trimethylarsine two methods were examined. In the first case arsenic trichloride *or tribromide was allowed to act on magnesium methyl iodide in* ethereal solution, the whole being cooled in ice. By this method apparently at least one other volatile compound, in addition to trimethylarsine, having a stronger and more penetrating odour, was produced. The second method was by the action of arsenic trichloride on zinc methyl in ethereal solution. Owing to the difficulty of separating the ether and the resulting trimethylarsine, it was found advisable to replace the ether by xylene, and then satisfactory yields of pure trimethylarsine, b. p. 51·9—52°/736 mm., D^{22} 1·124, were obtained.

When finely powdered selenium was added to the crude ethereal *solution of trimethylarsine prepared by the first method, trimethylarsine selenide*, $AsMe_3Se$, was obtained. It is very unstable in air, giving off an odour similar to that of trimethylarsine. W. G.

Process for the Preparation of Arsine Derivatives. André Job and Henri Guinot (Brit. Pat. 144806).—The nitriles of the general formula R_2AsCN, where R is a fatty or aromatic *group, are converted into amides and acids of the type* $AsR_2{\cdot}CO{\cdot}NH_2$ and $AsR_2{\cdot}CO_2H$ by the general methods for the hydration of nitriles. For example, cacodyl cyanide is converted into dimethylarsinoformic acid by boiling it with about three times its weight of 50% sulphuric acid for twelve hours. The acid is isolated through its calcium or barium salt and crystallised from acetone and alcohol. Diphenylarsinoformic acid is similarly obtained from diphenylarsine cyanide, or the amide may be first prepared by treating the cyanide in alkaline solution with the theoretical quantity of hydrogen peroxide, and be converted into the acid by subsequent treatment with nitrous acid. Diphenyl*arsinoformic acid is much less soluble in water than the dimethyl compound. It reddens blue litmus, and forms salts, the majority* of which are very soluble in water. G. F. M.

The Preparation of Zinc Methyl. R. R. Renshaw and C. E. Greenlaw (*J. Amer. Chem. Soc.*, 1920, **42**, 1472—1474).—For the preparation of a suitable zinc-copper couple it is recommended to mix nine parts of zinc powder passing a 30-mesh sieve with one part of copper precipitated from solution by zinc, and heat the mixture gradually in a current of hydrogen in a combustion tube, the tube being rotated rapidly, until the zinc turns first a yellow colour and then forms into little pellets of a tarnished lead colour. The heating is then stopped, the couple cooled in hydrogen and used. Methyl acetate is used as a catalyst for the preparation of zinc methyl, 1 c.c. being added to 110 grams of methyl iodide before it is run on to the zinc-copper couple. The mixture is left overnight and then heated at 60° next day, con-

densation being complete in about seven hours. It is noted that at ordinary temperatures zinc methyl iodide dissociates to give enough zinc methyl to cause the vapour above to inflame spontaneously when exposed to the air. W. G.

The Energy Content of Polymethylene Rings. WALTER HÜCKEL (*Ber.*, 1920, **53**, [*B*], 1277—1283).—The author has applied to polymethylene rings the considerations recently used by Fajans and von Steiger in calculating the heats of combustion of aliphatic and aromatic hydrocarbons (this vol., ii, 354, 355). The heat of combustion of the methylene group in each ring is obtained by *dividing the heat of combustion of the necessary compound by the* number of carbon atoms contained in it, and the difference between these values and 158 Cal. (the value for the CH_2 group in a normal carbon chain) is a measure of the abnormal energy content of the rings. In this manner, the values 170, 168·5, 165·5, 159, and 158 are obtained for the methylene group in ethylene, *cyclo*propane, *cyclo*butane, *cyclo*pentane, and *cyclo*hexane respectively. These results are in good accord with Baeyer's strain theory. Using the formula developed by Fajans (*loc. cit.*), the energy of the C–C linking in the various rings is calculated to 126, 127·2, 130·1, 136·5, 137·5, 138·5, and 139 in ethylene, *cyclo*propane, *cyclo*butane, *cyclo*pentane, *cyclo*hexane, *cyclo*heptane, and decahydronaphthalene respectively, the data being in agreement with Baeyer's strain theory as far as the lower members are concerned. The values obtained for methyl*cyclo*butane, methyl*cyclo*pentane, and *cyclo*heptane, however, require further explanation.

Much of the confusion which has existed with regard to the relative stability of different ring systems is due to inexact comparison. Thus, for example, it has been shown by Berthelot that the union of bromine with *cyclo*propane is accompanied by the development of 9·4 Cal. more than the union of bromine with propylene, and the conclusion is drawn that the *cyclo*propane ring is the more unstable. Actually, the processes are not completely similar, since different types of bond are broken; in the case of *propylene, a double bond is opened (energy consumption,* 126·5 Cal.), and the other passes into the normal linking (energy evolution, $137·5-126·5=11$ Cal.), there being thus a total consumption of 115·5 Cal. With *cyclo*propane, the calculated values are: consumption, 127; evolution, $2(137·5-127)=21$, or a total consumption of 106 Cal. The difference, therefore, is 9·5 Cal., which agrees excellently with Berthelot's experimental figure. H. W.

The Phenylpropinenes. R. LESPIEAU and GARREAU (*Compt. rend.*, 1920, **171**, 111—113).—By the action of benzyl chloride on monosodium acetylide, the principal product is the phenylpropinene, CPh⋮CMe. If the method of Lespieau and Bourguel (this vol., i, 520) is used, *epi*dibromohydrin gives with magnesium phenyl bromide *β-bromo-α-phenylpropylene*, $CH_2Ph·CBr{:}CH_2$, m. p. $-12·5°$, b. p. 102°/17 mm., D^0 1·39, which when treated

with alcoholic potassium hydroxide at 110° gives the propinene mentioned above. If *β*-bromo-*α*-phenylpropylene is brominated, it yields *ββγ-tribromo-α-phenylpropane*, b. p. 175—176°/18 mm. which when reduced with sodium in alcohol gives a *compound*, which with zinc in alcohol gives an acetylenic hydrocarbon, although the yields throughout are very small. If *epi*dibromo hydrin is brominated and the resulting tribromopropene,

$CHBr:CBr\cdot CH_2Br$,

is condensed with magnesium phenyl bromide in excess, a considerable yield of *γ-phenyl-Δ^α-propinene*, $CH_2Ph\cdot C:CH$, b. p. 70—71°/20 mm., is obtained, which gives *silver* and *copper* derivatives. The cuprous derivative when treated with excess of iodine gives *βγγ-tri-iodo-α-phenylpropylene*, $CH_2Ph\cdot CI:CI_2$, m. p. 84—85°. W. G.

Examination of Nitro-compounds by means of Titanium Chloride and Sulphate. C. F. van Duin (*Rec. trav. chim.*, 1920, **39**, 578—585).—It is recommended to replace the titanium chloride by titanium sulphate in Knecht's method for determining the nitro-nitrogen in nitro-compounds in the case of feebly substituted compounds.

The author has successfully used titanous chloride for the partial reduction of *s*-trinitrobenzene, obtaining a 50% yield of dinitroaniline.

From a study of the reduction of 2:3:4:6-tetranitroaniline and of trinitromethylnitroaminophenol by titanous chloride, it is argued that the structure of the nitro-group in position 3 is given by $\cdot NO_2$, and not by $\cdot O\cdot NO$. W. G.

The Action of the Grignard Reagent on Aromatic Nitro-compounds. Harry Hepworth (T., 1920, **117**, 1004—1012).

Experiments on Halogenation. The Direct Displacement of Negative Groups by Halogen in the Aromatic Series. I. The Displacement of the Nitro-group by Bromine. Surendra Nath Dhar (T., 1920, **117**, 993—1001).

The Replaceability of Halogens. I. Comparative Replaceability of Chlorine, Bromine, and Iodine in the Halogenonitrobenzenes. Hartwig Franzen and Erich Bockhacker (*Ber.*, 1920, **53**, [*B*], 1174—1179).—The data recorded with regard to the relative ease of replacement of the halogens in aromatic compounds are somewhat conflicting, and, as the observations were usually made for preparative purposes, are insufficiently exact to allow any generalisations on the subject. A series of comparative experiments with the halogenonitrobenzenes has therefore been undertaken, the present observations dealing exclusively with alcoholic solutions. In general, the substance (5*MM*) is mixed with the base—piperidine, diethylamine, ammonia, sodium ethoxide—(25*MM*), and either preserved at 0° or at the ordinary tempera-

ture, or heated at the boiling point of the solution or at 100°. The course of the reaction is followed by pouring the solution, after definite intervals of time, into water, adding nitric acid in excess, filtering from precipitated organic matter, and estimating the halogen acid as silver haloid. The results that have been obtained may be summarised as follows. In the cases of the action of diethylamine, piperidine, and sodium ethoxide on the 1-halogeno-2-nitrobenzenes and 1-halogeno-4-nitrobenzenes, iodine is least easily replaced. With diethylamine and piperidine, bromine is more readily replaced than chlorine, but whilst with sodium ethoxide this is also true in the case of *o*-chloronitrobenzene, the reverse holds with *p*-chloronitrobenzene. Reaction of 1-halogeno-2:4-dinitrobenzenes with ammonia, piperidine, aniline, and sodium ethoxide occurs least readily with the iodo-compounds; with ammonia and sodium ethoxide, chlorine is replaced more rapidly than bromine, whilst with piperidine and aniline, bromine reacts more readily than chlorine. There is no general parallelism between the strength of the base and its power of effecting replacement of halogens in the halogenonitrobenzenes in the sense that the stronger base reacts more rapidly than the weaker: the reverse can also be the case. H. W.

Some New Derivatives of Mesitylene and ψ-Cumene. CHARLES STANLEY GIBSON (T., 1920, **117**, 948—957).

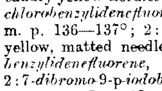
Some Nitro-derivatives of Naphthalene and Anthraquinone. SURENDRA NATH DHAR (T., 1920, **117**, 1001—1004).

The Fluorene Series. II. ADOLF SIEGLITZ (*Ber.*, 1920, **53**, [*B*], 1232—1241. Compare this vol., i, 27).—The condensation of fluorene with aromatic aldehydes has been further investigated. It is found that 2:7-dibromofluorene reacts with unexpected ease with aromatic aldehydes, yielding products which are solid and characterised by marked ability to crystallise, so that they are very suitable for the identification of the aldehydes. Unfortunately, it does not appear possible to extend the reaction to aliphatic aldehydes or ketones. The colour of the substituted fulvenes is uniformly deeper than that of the substances derived from fluorene itself, but the halochromic colorations with sulphuric acid in the new series are not characteristic. The following individual compounds are described: 9:9′-iso*phthalylidenedifluorene*, pale yellow leaflets, m. p. 178—179°; 9-p-*bromobenzylidenefluorene*, yellow needles, m. p. 144°; 9-m-*iodobenzylidenefluorene*, yellow, microscopic needles, m. p. 103°; 9-p-*iodobenzylidenefluorene*, pale yellow, flat prisms, m. p. 121°; 9-*piperonylidenefluorene*, yellow needles, m. p. 72—73° [*picrate*, dark red needles with green reflex, m. p. 194—195° (decomp.)]; 9-*anisylidenefluorene picrate*, red needles, m. p. 121° (decomp.); 9-*furylidenefluorene picrate*, dark red needles, m. p. 146—147° (decomp.).

2:7-Dibromofluorene, m. p. 164°, is conveniently prepared by the gradual addition of bromine to an ice-cold solution of fluorene

in chloroform. The condensation products are prepared by adding the calculated amount of the aldehyde dissolved in alcohol (20 c.c.) to a boiling solution of sodium (0·5 gram) and dibromofluorene (1·5 grams) in absolute alcohol (100 c.c.); the solution is rapidly heated to boiling, and subsequently preserved for a day, after which the product is separated; a red substance, probably 2:2′:7:7′-tetrabromo-αδ-dibiphenylene-$\Delta^{\alpha\gamma}$-butadiene, is formed as by-product. The following products are described: *2:7-dibromo-9-benzylidenefluorene*, long, pale yellow rods, m. p. 98—99°; *2:7-dibromo-9-o-methylbenzylidenefluorene*, orange-yellow leaflets, m. p. 141—142°; *2:7-dibromo-9-m-methylbenzylidenefluorene*, yellow prisms, m. p. 95—96°; *2:7-dibromo-9-p-methylbenzylidenefluorene*, yellow, matted needles, m. p. 140—141°; *2:7-dibromo-9-o-ethylbenzylidenefluorene*, yellow prisms and leaflets, m. p. 132—133°; *2:7-dibromo-9-m-ethylbenzylidenefluorene*, yellow rods, m. p. 82—83°; *2:7-dibromo-9-p-isopropylbenzylidenefluorene*, yellow needles, m. p. 116—117°; *2:2′:7:7′-tetrabromo-9:9′-isophthalylidenedifluorene*, slender, pale yellow needles, which do not melt below 280°; *2:7-dibromo-9-p-aldehydobenzylidenefluorene*, orange-yellow needles, m. p. 218—219°; *2:2′:7:7′-tetrabromoterephthalylidenedi-9:9′-fluorene*, dark orange leaflets, which do not melt below 300°; *2:7-dibromo-9-o-chlorobenzylidenefluorene*, canary-yellow needles and rods, m. p. 168—169°; *2:7-dibromo-9-m-chlorobenzylidenefluorene*, pale yellow, microcrystalline needles, m. p. 136—137°; *2:7-dibromo-9-p-chlorobenzylidenefluorene*, long, yellow, matted needles, m. p. 211—212°; *2:7-dibromo-9-m-bromobenzylidenefluorene*, small, yellow needles, m. p. 152—153°; *2:7-dibromo-9-p-iodobenzylidenefluorene*, orange-yellow needles, m. p. 207—208°; *2:7-dibromo-9-o-methoxybenzylidenefluorene*, orange-yellow leaflets, m. p. 154—155°; *2:7-dibromo-9-p-methoxybenzylidenefluorene*, deep yellow needles, m. p. 132—133°; *2:7-dibromo-9-piperonylidenefluorene*, yellow needles, m. p. 159—160°; *2:7-dibromo-9-o-nitrobenzylidenefluorene*, orange-yellow needles, m. p. 201—202°; *2:7-dibromo-9-m-nitrobenzylidenefluorene*, small, yellow crystals, m. p. 154—155°; *2:7-dibromo-9-p-nitrobenzylidenefluorene*, orange-yellow, microcrystalline powder, m. p. 195—196°; *2:7-dibromo-9-2′-chloro-5′-nitrobenzylidenefluorene*, yellow needles, m. p. 212—213° after softening at 190° (m. p. 216—218° after resolidification); *2:7-dibromo-9-cinnamylidenefluorene*, slender, deep yellow needles, m. p. 206—207°; *2:7-dibromo-9-furylidenefluorene*, long, greenish-yellow needles, m. p. 190—191°.

Ethyl oxalate condenses with 2:7-dibromofluorene in the presence of sodium ethoxide to form *ethyl 2:7-dibromofluoreneoxalate* (annexed formula), shining, yellow needles, m. p. 176°; the substance gives a brown coloration with ferric chloride, and yields a *benzoyl* derivative, canary-yellow rods, m. p. 152—153°.



H. W.

*cyclo***Hexylamines. II.** A. SKITA and H. ROLFES (*Ber.*, 1920, **53**, [*B*], 1242—1255. Compare Skita and Berendt, this vol., i, 27). —In connexion with Skita's process for the reduction of aromatic amines to *cyclo*hexylamines, the general behaviour of the latter class of substances has been more fully investigated.

[With KARL HILS and GUSTAV KIRCHHOFF.]—*Ammonium di*cyclo*hexyl dithiocarbamate*, $C_6H_{11}\cdot NH\cdot CS\cdot S\cdot NH_3\cdot C_6H_{11}$, m. p. 160°, is readily prepared by the direct union of *cyclo*hexylamine and carbon disulphide; it is converted by distillation with an aqueous solution of mercuric chloride into cyclo*hexylthiocarbimide*, b. p. 219°/746 mm., which may also be obtained by the distillation of *di*cyclo*hexylthiocarbamide*, cubes, m. p. 180—181°, with glacial phosphoric acid. *cyclo*Hexylthiocarbimide combines with ammonia to yield cyclo*hexylthiocarbamide*, $NH_2\cdot CS\cdot NH\cdot C_6H_{11}$, m. p. 161—162°, with aniline to give *phenyl*cyclo*hexylthiocarbamide*, m. p. 150—151°, and with absolute alcohol at 100° to form cyclo*hexylthiourethane*, m. p. 45—46°.

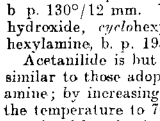
*Di*cyclo*hexylcarbamide*, m. p. 229—230°, is obtained from *cyclo*hexylamine and carbonyl chloride, and is converted by phosphoric oxide into cyclo*hexylcarbimide*, $C_6H_{11}\cdot N:C:O$, b. p. 175°/750 mm.; the latter is transformed by ammonia, aniline, and ethyl alcohol into cyclo*hexylcarbamide*, m. p. 184°, *phenyl*cyclo*hexylcarbamide*, colourless needles, m. p. 182°, and cyclo*hexylurethane*, m. p. 57°.

*cyclo*Hexylamine is converted by methyl sulphate in warm ethereal solution into cyclo*hexylamine methyl sulphate*, m. p. 103°, and a basic portion, which, after purification through the *acetyl* derivative, b. p. 249°/740 mm., or the *benzoyl* derivative, needles, m. p. 76°, yields *N*-methyl*cyclo*hexylamine, b. p. 147°, identical in all respects with the product obtained previously (*loc. cit.*) by the catalytic hydrogenation of methylaniline. It was further identified by conversion into the *picrate*, m. p. 170°, and into *nitroso*-N-*methyl*cyclo*hexylamine*, yellow liquid, b. p. 121°/12 mm. (*hydrochloride*, needles, m. p. 176°). *N*-Dimethyl*cyclo*hexylamine, b. p. 165°, is prepared in 80% yield by the action of formic acid and formaldehyde on *cyclo*hexylamine at 120°; the *picrate* has m. p. 181°. The base is converted by methyl iodide into *trimethyl*cyclo*hexylammonium iodide*, needles, m. p. 277°, which is transformed by silver oxide into the corresponding *hydroxide*, which decomposes into tetrahydrobenzene, trimethylamine, and water when its aqueous solution is evaporated. When treated with nitrosyl chloride in cold ethereal solution, *N*-dimethyl*cyclo*hexylamine undergoes a remarkable change, whereby *N*-nitroso-*N*-methyl*cyclo*hexylamine is produced; the latter is reduced by tin and hydrochloric acid to *N*-methyl*cyclo*hexylamine. A similar instance is presented by *N*-methyldi*cyclo*hexylamine, $C_6H_{11}\cdot NMe\cdot C_6H_{11}$, which with nitrosyl chloride gives *nitrosodi*cyclo*hexylamine*, $C_6H_{11}\cdot N(NO)\cdot C_6H_{11}$, m. p. 105°, which is reduced to di*cyclo*hexylamine by zinc and hydrochloric acid.

Ethyl iodide reacts readily with *cyclo*hexylamine, giving *N*-ethyl*cyclo*hexylamine, identical with the product obtained by the cata-

lytic reduction of ethylaniline (*loc. cit.*); the *benzoyl* and acetyl derivatives have b. p.'s 201° and 256°/740 mm. respectively, whilst the *picrate*, yellow crystals, and *hydrochloride*, have m. p.'s 133° and 184° respectively. *Nitroso*-N-*ethyl*cyclo*hexylamine* is an oil, b. p. 130°/12 mm. When treated with ethyl iodide and potassium hydroxide, *cyclo*hexylamine is transformed into *N*-diethyl*cyclo*hexylamine, b. p. 193°.

Acetanilide is but little attacked by hydrogen under conditions similar to those adopted for the reduction of aniline to *cyclo*hexylamine; by increasing the concentration of the catalyst and raising the temperature to 70—80°, it can be completely hydrogenated to acetyl*cyclo*hexylamine, m. p. 107°. Under similar conditions, the isomeric acetotoluidides can be completely converted into their hexahydro-derivatives; *acetyl-2-methyl*cyclo*hexylamine* has b. p. 154°/20 mm., m. p. 50°, the corresponding *3-derivative* has b. p. 152°/18 mm., m. p. 74—75°, whilst the *4-compound* has b. p. 152°/12 mm., m. p. 77—78°. *p*-Ethoxyacetanilide is hydrogenated with remarkable ease, but the product is acetyl*cyclo*hexylamine, m. p. 106—107°. The elimination of the ethoxy-group is the more noteworthy since anisole and phenetole are reduced to *cyclo*hexyl methyl ether, b. p. 140°/740 mm., and *cyclo*hexyl ethyl ether, b. p. 144—145°/738 mm., under precisely similar conditions. Anisidine and phenetidine are, however, converted into a mixture of di*cyclo*hexylamine and *cyclo*hexylamine (small quantities of the latter are very rapidly and conveniently identified by conversion into p-*toluenesulphon*cyclo*hexylamide*, $C_6H_4Me\cdot SO_2\cdot NH\cdot C_6H_{11}$, m. p. 86°). A similar mixture of bases is obtained from *p*- and *m*-aminophenol; *o*-aminophenol gives a mixture of *cyclo*hexylamine and *dodecahydrophenoxazine* (annexed formula), m. p. 103—104° (*benzoyl* derivative, pyramids,



m. p. 160—161°). H. W.

Crystalline Form of 2 : 4-Dichloro-3-nitroacetanilide. Maria De Angelis (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 247—251).—This compound is dimorphous; both the α- and β-modifications form crystals belonging to the prismatic class of the monoclinic system; for the former, $a:b:c=1{\cdot}1507:1:1{\cdot}1348$, $\beta=66°23'$, and for the latter, $a:b:c=1{\cdot}5792:1:1{\cdot}0952$, $\beta=62°23{\cdot}5'$. T. H. P.

Catalysts which Promote Reaction between Aniline and Ethyl Alcohol. T. B. Johnson, A. J. Hill, and J. J. Donleavy (*J. Ind. Eng. Chem.*, 1920, **12**, 636—644).—No alkylation results when aniline is heated with ethyl alcohol in an autoclave in the presence of calcium oxide. Aniline hydrochloride heated with ethyl alcohol for eight hours in an autoclave at 175—180°, in the presence of sodium bromide, cupric chloride, and calcium chloride, gives good yields of diethylaniline containing only about 5% of mono-

hylaniline. Substitution of aniline for an equivalent quantity f *aniline hydrochloride* yields a product largely composed of monohylaniline. Zinc chloride probably has a dealkylising action as ell as a dehydrating effect, and is less effective as a catalyst than alcium chloride, whilst potassium iodide is slightly more effective ian sodium bromide. The use of 95% alcohol instead of absolute thyl alcohol causes the yield of diethylaniline to be lowered by bout 7%. The addition of the sodium bromide has the effect of wering the amount of monoethylaniline by about 2%, whilst yridine has a negative catalytic action, and raises it by about 11% ompare *J. Soc. Chem. Ind.*, 1920, September). C. A. M.

Catalytic Hydrogenation of Nitriles; Mechanism of the ormation of Secondary and Tertiary Amines. GEORGES IGNONAC (*Compt. rend.*, 1920, **171**, 114—117).—When benzoitrile is hydrogenated in absolute alcohol in the presence of nickel s catalyst at the ordinary temperature (compare this vol., i, 442), ie operation being interrupted when one molecule of hydrogen has een fixed, the product consists of one part of benzylamine and -2·5 parts of benzylidenebenzylamine, $CHPh\colon N\cdot CH_2Ph$, the itter, if the hydrogenation is continued, being converted into ibenzylamine. The course of the reaction is considered to be that enzaldimine is first formed, and that this then rapidly condenses ith the elimination of ammonia,

$$3CHPh\colon NH = NH_3 + CHPh(N\colon CHPh)_2,$$

nd that the condensation product then undergoes hydrogenation, iving benzylamine and benzylidenebenzylamine.

Under similar conditions, *o*-toluonitrile gives *o*-methylbenzylamine nd *o-methylbenzylidene-o-methylbenzylamine*, b. p. 170—171°/ mm., and *p*-toluonitrile gives *p*-methylbenzylamine and *p-methylenzylidene-p-methylbenzylamine*, m. p. 83—84°, b. p. 160°/3·5 mm. W. G.

Hydrogenation in the Naphthalene Series. F. M. ROWE *J. Soc. Chem. Ind.*, 1920, **39**, 241—246).—α-Naphthylamine is educed by sodium and amyl alcohol to *ar*-tetrahydro-α-naphthylmine, but, in the presence of ethyl or butyl alcohol, only dihydroerivatives are formed. Preliminary experiments indicate that this ifference cannot be ascribed solely to differences in temperature of he experiment. A similar result is observed when reduction is ffected in the presence of an indifferent solvent, such as oluene or solvent naphtha (compare D.R.-P. 305347, 306724). more extended study shows that α-naphthylamine is reduced y sodium and an alcohol to 5 : 8-dihydro-1-naphthylamine; he latter, under suitable conditions of temperature and alkali lkyloxide concentration, undergoes isomerisation to 7 : 8-dihydro-1-aphthylamine, which, unlike the 5 : 8-isomeride, is further reduced o *ar-tetrahydro-α-naphthylamine*. The failure to obtain the tetraydro-compound when amyl alcohol was not used is probably to be xplained by the absence of conditions suitable for the isomerisa-

tion. Reduction of naphthalene takes place similarly to that of α-naphthylamine; 1:4-dihydronaphthalene is initially formed, which, under suitable conditions, is isomerised to 1:2-dihydronaphthalene and then reduced to tetrahydronaphthalene.

The direct hydrogenation of naphthalene and α-naphthylamine has also been studied, the experiments being performed by bubbling hydrogen at the ordinary pressure through the purified substance, either molten or dissolved in a suitable solvent, in presence of nickel deposited on kieselguhr, in a glass vessel fitted with a condenser and an agitator capable of being driven at a high speed. Temperatures varying from 100° to the respective boiling points of naphthalene and α-naphthylamine were used with these substances in the absence of a solvent without result, except that there was an appreciable evolution of ammonia in the latter case, particularly at the higher temperatures. Negative results were also obtained with α-naphthylamine dissolved in boiling light petroleum, toluene, or solvent naphtha. The base, however, was reduced in boiling ethyl-alcoholic solution or, preferably, in boiling mixtures of ethyl alcohol with toluene or solvent naphtha; in the latter circumstances, 5:8-dihydro-α-naphthylamine was quantitatively formed, but the further reduction to tetrahydro-α-naphthylamine was not satisfactorily accomplished. Similarly, naphthalene could be hydrogenated in boiling ethyl-alcoholic solution, a mixture of products being invariably obtained, the main constituent of which is 1:4-dihydronaphthalene; prolongation of the action or treatment of 1:4-dihydronaphthalene in boiling ethyl-alcoholic solution led to the formation of some tetrahydronaphthalene, together with a mixture of liquids of lower boiling point which was not examined more closely, but probably consisted of more completely saturated derivatives. H. W.

Spontaneous Decomposition of α-Aminophenyl-α-naphthylmethane. II. S. BERLINGOZZI (*Gazzetta*, 1920, **50**, i, 321—325. Compare this vol., i, 480).—α-Aminophenyl-α-naphthylmethane undergoes spontaneous decomposition at the ordinary temperature, with liberation of ammonia and formation of *di-(naphthylbenzyl-)amine*, $NH(\cdot CHPh\cdot C_{10}H_7)_2$, which forms minute, shining, white crystals, m. p. 181°. It is shown that the product, m. p. 121°, described by Busche and Leefhelm (A., 1908, i, 152) as α-aminophenyl-α-naphthylmethane, consists of a mixture of the latter with di-(naphthylbenzyl-)amine. T. H. P.

Oxynitration of Benzene [Formation of Nitrophenols]. LÉO VIGNON (*Bull. Soc. chim.*, 1920, [iv], **27**, 547—550).—To obtain the best yield of nitrophenols in the action of nitric acid and mercuric nitrate on benzene it is advisable to use an excess of benzene, and the following proportions are recommended: 1000 grams of nitric acid (D 1·29—1·325), 25 grams of mercuric nitrate, and 500 grams of benzene, the mixture being heated on a water-bath for five to seven hours. W. G.

Derivatives of Diphenyl Ether. ALFRED N. COOK, WM. C. EVANS, and DANIEL SHERK (*Proc. S. Dak. Acad. Sci.*, 1917, **2**. 21—25).—2:4-*Dinitrophenyl* 6-*propyl*-m-*tolyl ether*,

$$C_6H_3(NO_2)_2 \cdot O \cdot C_6H_3MePr,$$

sulphur-yellow needles, m. p. 64°, obtained by heating equal molecular quantities of potassium thymolate and 1-bromo-2:4-dinitrobenzene, yields on sulphonation a *monosulphonic acid*, pearly crystals (*lead* salt; *barium* salt with $5 \cdot 5H_2O$). 2-*Nitrophenyl* 5 *propyl*-o-*tolyl ether*, brownish-red liquid, b. p. 222°/20 mm., forms a *sulphonic acid*, crystals with $2H_2O$, m. p. 223—227° (decomp.), of which the *barium*, *calcium*, and *lead* salts crystallise with 3, 6, and $8H_2O$ respectively. CHEMICAL ABSTRACTS.

Derivatives of the Sulphone of o-**Cresol** (o-**Hydroxytolylsulphone**). FRÉDÉRIC REVERDIN and ANDRÉ ROETHLISBERGER (*Helv. Chim. Acta*, 1920, **3**, 486—492).—The authors have prepared o-hydroxytolylsulphone by Zehenter's method (A., 1912, i, 444), and have studied certain of its derivatives.

The acetyl compound agrees in properties with Tassinari's product (A., 1889, 245). The *benzoyl* derivative, $SO_2(C_6H_3Me \cdot OBz)_2$, prepared by either Schotten and Baumann's or Reverdin's method (A., 1918, i, 536), forms colourless, prismatic crystals, m. p. 183—184°. The dinitro-derivative, m. p. 243° (compare Zehenter, *loc. cit.*), yields an *acetyl* compound, $SO_2(NO_2 \cdot C_6H_2Me \cdot OAc)_2$, which forms deep yellow crystals, m. p. 204—205°, and a *benzoyl* compound, $SO_2(NO_2 \cdot C_6H_2Me \cdot OBz)_2$, m. p. 179—180°.

When treated with sulphuric acid (20% SO_3), the dinitro-derivative is converted into an *isomeride*, $C_{14}H_{12}O_8N_2S$, which forms yellow crystals, m. p. 209—210°, and yields an *acetyl* derivative, crystallising in pale yellow plates, m. p. 200—201°.

Nitration of the acetyl derivative of the sulphone yields partly the acetyl dinitro-compound, melting at 243°, but is incomplete, and, if carried further, is accompanied by partial scission of the molecule. Nitration of the benzoyl derivative yields mainly a m-nitrobenzoyl-o-cresolsulphone, the nitro-group being introduced into the benzoyl residue.

Reduction of the dinitro-derivative, m. p. 243°, by means of tin and hydrochloric acid gives a double chloride of tin and the aminosulphone; the free *aminosulphone* forms pale brown needles, m. p. 212° (decomp.), is readily oxidised, gives solutions which colour in the air and yield a deep brown coloration with ferric chloride solution, and furnishes a highly stable *diazo*-derivative, crystallising in yellow needles. The compound obtained on reduction of the isomeric dinitro-compound, m. p. 209—210°, is not oxidised in solution by atmospheric oxygen, and yields a less stable diazo-derivative. T. H. P.

Derivatives of Trihalogen Tertiary Butyl Alcohol. III. The Benzoic Acid Ester of Trichloro-*tert.*-butyl Alcohol or Chloretone Benzoic Ester. T. B. ALDRICH (*J. Amer. Chem. Soc.*, 1920, **42**, 1502—1507. Compare A., 1916, i, 115; 1917, i, 77; 1919, i, 62).—A repetition of the work of Willgerodt and Dürr

(compare *J. pr. Chem.*, 1889, [ii], **39**, 286). It is now found when molecular proportions of benzoyl chloride and chlor (trichloro-*tert.*-butyl alcohol) are heated together on a water- until hydrogen chloride ceases to be given off, trichloro-*tert.*-l benzoate is obtained, and may be isolated in a crystalline f m. p. 34—35°. It may be distilled under reduced pressure v out appreciable decomposition, and is not readily hydrolysed, b much more stable than other esters of this alcohol. Pharn logical tests indicate that it possesses less hypnotic or anæstl properties, and is less toxic than the esters studied thus far *cit.*). W. (

Amino-alcohols. Action of Amines on the Mono-es (Acetates and Benzoates) of Chlorohydrins. E. Fourneau (Mme) P. Ramart-Lucas (*Bull. Soc. chim.*, 1920, [iv], 550—557).—Sodium benzoate acts on α-chloropentan-γ-ol in presence of potassium iodide to give *α-benzoyloxypentan-* b. p. 171°/11 mm., 181°/20 mm., which with thionyl chlorid pyridine solution yields *γ-benzoyloxypentan-α-ol*, b. p. 165—1(17 mm., 157—159°/12 mm. This chloro-ester when warmed v dimethylamine in benzene solution gives α-dimethylamin benzoyloxypentane, b. p. 170°/16 mm., which may also be obtai by the action of benzoyl chloride on α-dimethylaminopentan-γ When α-chloropentan-γ-ol is heated for four hours at 160—1 with potassium acetate it yields *γ-acetoxypentan-α-ol*, b. 113—114°/12 mm., which, with thionyl chloride, gives *α-chl γ-acetoxypentane*, b. p. 84—86°/14 mm. This chloroacetate v dimethylamine gives a mixture of bases, from which α-dimet amino-γ-acetoxypentane can be isolated. γ-Chloro-α-phenylpro β-ol with sodium benzoate gives a mixture of two benzoates, f which the chloro-compound can be prepared, and this v dimethylamine gives two bases, namely, γ-dimethylamino-α-phe propan-β-ol, b. p. 153°/40 mm., and its benzoate, b. p. 22 20 mm.

γ-Chloro-α-phenylpropan-α-ol gives with sodium benzoat *benzoate*, b. p. 230°/12 mm., which when treated with thi chloride, and then with dimethylamine, yields *γ-dimethylamin phenylpropyl benzoate*, b. p. 230°/15 mm., giving a *hydrochlor* m. p. 146°. W. G

The Preparation of *o*-Nitrobenzoic Acid. Marie Rei and Elizabeth Stewart Gatewood (*J. Amer. Chem. Soc.*, 1' **42**, 1475—1478).—The mixed *o*- and *p*-nitrotoluenes obtai from the nitration of toluene were oxidised by alkaline perm ganate in concentrated solution (compare Bigelow, this vol., i, The *o*- and *p*-nitrobenzoic acids were isolated by conversion their methyl esters, which were then separated by fracti distillation under reduced pressure. W. G

***o*-Sulphobenzoic Anhydride and Benzamide- and Met benzamide-*o*-sulphonic Acids.** H. J. Taverne (*Rec. trav. ch* 1920, **39**, 542—548).—*o*-Sulphobenzoic anhydride was prepared

the interaction of potassium hydrogen sulphobenzoate and phosphorus pentachloride, and by the action of acetyl chloride on the free acid. The anhydride prepared by either method had m. p. 130°, and molecular-weight determinations showed it to be an internal anhydride. By the action of dry ammonia on its benzene solution, it gave ammonium benzamide-*o*-sulphonate, from which the corresponding *barium* salt, $(NH_2\cdot CO\cdot C_6H_4\cdot SO_3)_2Ba,6H_2O$, was obtained, and this, on decomposition with dilute sulphuric acid, gave the free acid, m. p. 186°, giving a silver salt,

$$NH_2\cdot CO\cdot C_6H_4\cdot SO_3Ag,H_2O.$$

When a benzene solution of *o*-sulphobenzoic anhydride is saturated with methylamine, a crystalline precipitate of *methylammonium methylbenzamide-o-sulphonate*,

$$NHMe\cdot CO\cdot C_6H_4\cdot SO_3NH_3Me,$$

m. p. 189—190°, is obtained. This gives the corresponding *barium* salt, $(C_8H_8O_4NS)_2Ba,4H_2O$, which, on decomposition with sulphuric acid, gives *methylbenzamide-o-sulphonic acid*, m. p. 167—169°.

W. G.

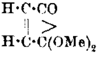
Catalytic Hydration of Nitriles. A. MAILHE (*Compt. rend.*, 1920, **171**, 245—247).—Nitriles may be converted into the corresponding acids by passing their vapours, along with water vapour, over thorium oxide at a temperature of 420°. W. G.

Boiling Points of Esters of Stereoisomeric Cinnamic Acids. R. STOERMER and KARL SANDOW (*Ber.*, 1920, **53**, [*B*], 1283—1289).—It was observed by Stoermer, Grimm, and Laage (A., 1917, i. 647) that the esters of *cis*-cinnamic acids uniformly boil about 12—15° lower than the esters of the corresponding stereoisomeric *trans*-acids, and that, as far as the evidence was available, this relationship held good even in those cases in which the *cis*-acid had a higher melting point than the *trans*-acid. The number of such instances was, however, somewhat restricted; in order, therefore, to secure further evidence on this point, the authors have prepared a further series of such pairs of acids, and have found their previous observation completely confirmed. The boiling points of the esters of stereoisomeric cinnamic acids appear to be a valuable criterion of the adherence of the free acid to the *allo*-series or otherwise. The alkyloxy-β-methylcinnamic acids are obtained from 4-methylcoumarin by fission and subsequent alkylation, or by transformation of the *cis*-forms primarily obtained into the corresponding *trans*-forms by concentrated potassium hydroxide solution. Esterification of the acids is conveniently effected with methyl or ethyl sulphate in alkaline solution. The following substances are described: *trans-o*-hydroxy-β-methylcinnamic acid, m. p. 160° (methyl ester, m. p. 143°); *trans-o*-methoxy-β-cinnamic acid (I), m. p. 96° (compare Stoermer, Grimm, and Laage, *loc. cit.*), *methyl* ester, b. p. 178—179°/28 mm.; *cis-o*-methoxy-β-methylcinnamic acid (II), m. p. 123°, *methyl* ester, b. p. 164°/

(I)	(II)
$OMe\cdot C_6H_4\cdot CMe$	$Me\cdot C\cdot C_6H_4\cdot OMe$
$H\cdot C\cdot CO_2H$	$H\cdot C\cdot CO_2H$
(I).	(II).

28 mm., m. p. 44°; trans-o-*ethoxy-β-methylcinnamic acid*, m. p. 111—112°, *methyl* ester, b. p. 160—161°/13 mm., m. p. 43°, *ethyl* ester, m. p. 53°, *amide*, m. p. 97°; cis-o-*ethoxy-β-methylcinnamic acid*, m. p. 138°, *methyl* ester, b. p. 148—148·5°/13 mm., *ethyl* ester, b. p. 152°/11 mm., *amide*, m. p. 118°; trans-o-n-*propoxy-β-methylcinnamic acid*, slender needles, m. p. 72°, *methyl* ester, b. p. 177°/20 mm.; cis-o-n-*propoxy-β-methylcinnamic acid*, m. p. 108°, *methyl* ester, b. p. 167°/20 mm.; trans-o-n-*butoxy-β-methylcinnamic acid*, colourless needles, m. p. 57°, *methyl* ester, b. p. 187—188°/24 mm.; cis-o-n-*butoxy-β-methylcinnamic acid*, m. p. 74°, *methyl* ester, b. p. 175°/24 mm. H. W.

Boiling Points of Esters of Stereoisomeric Unsaturated Acids. R. Stoermer and H. Kirchner (*Ber.*, 1920, **53**, [*B*], 1289—1299).—In previous communications (Stoermer, Grimm, and Laage, A., 1917, i, 647, Stoermer and Sandow, preceding abstract) it has been shown that the esters of the *cis*-form of stereoisomeric unsaturated cinnamic acids have a lower boiling point than the corresponding *trans*-compounds. The observations are now extended to the halogenated cinnamic acids, and the same regularity is observed in all cases in which the configuration of the acids can be regarded as definitely elucidated. In all, therefore, nineteen pairs of stereoisomeric esters have been investigated without leading to the discovery of an exception to the rule. Up to the present, however, only aromatic compounds have been considered; an attempt is therefore made to extend the observations to aliphatic compounds, and fumaric and maleic esters are chosen by reason of the close analogy in chemical behaviour of the phenyl and carboxyl groups. In this case, however, an exception appears to be presented which leads the authors to consider that methyl maleate may possibly have the annexed constitution;



a certain amount of evidence in favour of this view is derived from spectrochemical observations and from analogy to the corresponding chlorides. The melting point of the free acids appears to be a very uncertain criterion of their adherence to the *cis*- or *trans*-series; still less reliance can be placed on the melting points of their esters or amides in this respect. It is interesting to note that the position of the halogen atom in the α- and β-halogenated acids is practically without influence on the boiling points of the esters. The following compounds are described: *trans*-α-chlorocinnamic acid, m. p. 33—34°, *methyl* ester, b. p. 167° (corr.)/28 mm., 108—109°/0·5 mm.; *methyl* cis-*α-chlorocinnamate*, b. p. 153—154°/28 mm., 98—99°/0·6 mm.; methyl *trans*-α-bromocinnamate, m. p. 23°, b. p. 177—178° (corr.)/23 mm., 120—121°/0·6 mm.; *methyl* cis-*α-bromocinnamate*, b. p. 167·5—168·5° (corr.)/26 mm., 111°/0·6 mm.; trans-*α-chlorocinnamamide*, m. p. 121°, b. p. 216—217°/12 mm. (with partial sublimation), 158—160°/0·6 mm.; cis-*α-chlorocinnamamide*, m. p. 134°, b. p. 210°/13 mm., 153—154°/0·6 mm.; *trans*-α-bromocinnamamide,

m. p. 117—118°, b. p. 212—213°/13 mm. (partial decomp.); *cis-α-bromocinnamamide*, m. p. 129°, b. p. 215—216°/13 mm. The α-iodocinnamic acids (compare Bougault, A., 1916, i, 817) are obtained by the action of a solution of iodine in potassium iodide on the semicarbazone of phenylpyruvic acid in the presence of alkali, and are separated by taking advantage of the differences in their strengths; the *trans*-acid forms colourless leaflets, m. p. 162—163°, and yields a *methyl* ester, b. p. 132—133° (corr.)/0·4 mm., whilst the *cis*-acid forms yellow crystals, m. p. 110—111°, and gives a *methyl* ester, b. p. 114—115° (corr.)/0·4 mm. *Methyl* trans-*β-chlorocinnamate*, m. p. 29°; *methyl* cis-*β-chlorocinnamate*, m. p. 34°, b. p. 96—97° (corr.)/0·5 mm.; *methyl* trans-*β-bromocinnamate*, b. p. 122°/0·6 mm.; *methyl* cis-*β-bromocinnamate*, colourless needles, m. p. 56°, b. p. 110—111°/0·6 mm.; *methyl* trans-*αβ-dichlorocinnamate*, b. p. 121°/0·6 mm.; *methyl* cis-*αβ-dichlorocinnamate*, b. p. 113°/0·6 mm., *methyl* trans-*αβ-dibromocinnamate*, hexagonal rods, m. p. 64—65°, b. p. 138°/0·5 mm.; *methyl* cis-*αβ-dibromocinnamate*, b. p. 124°/0·5 mm.

Attempts to obtain *cis*-β-ethoxycinnamic acid are described. On one occasion a small amount of an acid, m. p. 78°, was isolated from the products of hydrolysis of ethyl β-ethoxycinnamate, which is possibly the desired substance, but the preparation could not be repeated. *trans*-β-Ethoxycinnamic acid is extensively decomposed when its solution in benzene is exposed to ultra-violet light, ethoxystyrene being produced. Under similar treatment, the ethyl ester is considerably resinified, but on distillation of the product a fraction of lower boiling point was obtained which yielded an acid, m. p. 70—80°, in small amount. Sodium β-ethoxycinnamate became completely resinified when illuminated. Similar observations with β-phenoxycinnamic acid and its ester are recorded. H. W.

Optically Active Cinnamic Acids and the Cinnamates of Tartaric Acid which are Produced at the Formation of the Former. EMIL ERLENMEYER and GUSTAV HILGENDORFF (*Biochem. Zeitsch.*, 1920, **108**, 79—123).—Tartaric acid was fused with cinnamoyl chloride, cinnamic anhydride, and cinnamic acid respectively at 168—170°. The cinnamic acid was extracted from the fused mass with light petroleum. The acid thus obtained was optically active. The highest activity was manifested by the cinnamic acid obtained by extracting the product of fusion of cinnamic anhydride with tartaric acid. The residues obtained by extracting the fused masses with light petroleum were further extracted with ether, yielding a colloidal fraction which was again fractionated either by extraction with benzene or by treating it with sodium carbonate, gradually acidifying, and extracting the successive fractions with ether. The various fractions thus obtained containing mixtures of cinnamates showed a carbon content varying from 55·76%, which represents the carbon content of the monocinnamates, to 64·39%, which is that of the dicinnamates. The lowest rotation was shown by the cinnamates obtained from the fusion

with cinnamic acid, the highest rotation by those obtained with cinnamoyl chloride. An intermediate value was shown by cinnamates from the anhydrides. This is explained by the presence of large quantities of the highly active dicinnamate in the chloride mixture and the absence of the less active monocinnamate, which is, however, present in the anhydride fusion and more so in the cinnamic acid fusion. A colloidal monodicinnamate (α_D $-120°$ approximately) was also obtained from the cinnamoyl chloride fusion. Cinnamates with a similar number of carbon atoms, but of a higher rotation, were obtained from the anhydride and from the cinnamic acid fusions. These masses also yielded a fraction of the same carbon content as the dicinnamates, but of a considerably lower rotation. It is suggested that the optical activity of the cinnamic acid extracted from the cinnamic anhydride fusion is due to the "induction" influence of the cinnamates formed. S. S. Z.

Benzylic Acid and Aldehydes. A. BISTRZYCKI and BRUNO BRENKEN (*Helv. Chim. Acta*, 1920, **3**, 468—472).—The authors have shown (see this vol., i, 630) that, whereas 1 mol. of thioglycollic acid condenses with 2 mols. of an aldehyde, 1 mol. of thiobenzylic acid condenses with only 1 mol. of an aldehyde. The experiments now described show that benzylic acid acts on aldehydes in the same way as aliphatic hydroxy-acids or thiobenzylic acid. According to Wallach (A., 1878, 288), the first stage in the formation of chloralide by the interaction of trichlorolactic acid and anhydrous chloral consists in the conversion of the acid into trichlorolactide, which then reacts with the chloral. The authors, however, consider it more probable that the reacting compounds first form an additive compound comparable with chloral alcoholate, decomposition with loss of water then taking place:

$$CO_2H\cdot CH(OH)\cdot CCl_3 + CCl_3\cdot CHO = CO_2H\cdot CH(CCl_3)\cdot O\cdot CH(OH)\cdot CCl_3 = CCl_3\cdot CH\!<\!\begin{matrix}O-CH\cdot CCl_3\\ CO\cdot O\end{matrix} + H_2O.$$

The *methylene ether ester of benzylic acid*, $CPh_2\!<\!\begin{matrix}O-CH_2\\ CO\cdot O\end{matrix}$, prepared by the interaction of benzylic acid and formaldehyde, forms transparent, rhomboidal plates often with truncated angles, softening a little below its m. p., 43—44°. The powdered substance is converted into deep blue flocks by concentrated sulphuric acid, the latter turning first green and then colourless. It is appreciably more stable than the corresponding ester of glycollic acid (compare de Bruyn and van Ekenstein, A., 1902, i, 76; 1903, i, 149), from which it is derived.

The *benzylidene ether ester*, $CPh_2\!<\!\begin{matrix}O-CHPh\\ CO\cdot O\end{matrix}$, obtained from benzylic acid and benzaldehyde, crystallises in bundles of flat, microscopic prisms, m. p. 94—95°, and dissolves in concentrated sulphuric

acid, giving a violet-red solution, which shows a faint greenish-brown fluorescence. This compound also exhibits marked stability.

Attempts to couple acetone with benzylic acid were unsuccessful.

T. H. P.

Derivatives of Gallic Acid. I. Synthesis of 4-Hydroxy-3 : 5-dimethoxyphthalic Acid. RUPCHAND LILARAM ALIMCHANDANI and ANDREW NORMAN MELDRUM (T., 1920, **117**, 964—970).

Improved Process for the Elimination of Carboxyl Groups. JAMES ERNEST MARSH (Brit. Pat. 144897).—Carboxyl groups may be eliminated from organic acids, particularly hydroxy-aromatic acids, such as gallic acid, by heating the acid with a dry metallic salt, preferably an alkali haloid. The reaction is advantageously carried out under reduced pressure, and, if the product is volatile, it may be conducted in a vacuum still, so that the decomposition of the acid and the recovery of the product by distillation proceed simultaneously. For instance, pyrogallol is obtained in a technically pure condition by distilling a mixture of gallic acid with half its weight of sodium chloride at 250° and 15 mm. pressure. The yield amounts to 95% of the theoretical. G. F. M.

Phenolphthalein. F. UTZ (*Süddeut. Apoth. Zeit.*, 1920, **60**, 430—431, 442—444; from *Chem. Zentr.*, 1920, iv, 155).—The amounts of phenolphthalein in grams contained in 100 c.c. of a warm saturated solution of the substance in the various solvents are as follows: ethyl alcohol, 20·91; methyl alcohol, 14·18; acetone, 26·39; chloroform, 3·06; carbon disulphide, 0·18; ether, 5·92; light petroleum, 0·18 or 1·06, depending on the boiling point of the solvent; benzene, 0·16; carbon tetrachloride, traces; xylene, 0·18; toluene, 0·61; nitrobenzene, 4·41; ethyl acetate, 6·57. Water (10 c.c.) dissolves 0·0002 gram of phenolphthalein at the ordinary temperature, and about ten times this amount when warmed.

H. W.

Bromohydrins and Dibromo-derivatives obtained from the Alkylallylacetophenones, $COPh\cdot CHR\cdot CH_2\cdot CH:CH_2$ and $COPh\cdot CRR'\cdot CH_2\cdot CH:CH_2$. A. HALLER and (MME) P. RAMART-LUCAS (*Compt. rend.*, 1920, **171**, 144—148).—The dialkylacetophenones studied when treated with bromine in chloroform solution give bromohydrins, the intermediate dibromo-derivatives being unstable and decomposed by moisture. The authors favour the constitution (formula I) for the

$$COPh\cdot CRR'\cdot CH_2\cdot CH:CH_2 + Br_2 \longrightarrow COPh\cdot CRR'\cdot CH_2\cdot CHBr\cdot CH_2Br$$

(the dibromo-derivative, with H_2O, gives either I or II:)

$$\underset{\text{(I.)}}{COPh\cdot CRR'\cdot CH_2\cdot CH(OH)\cdot CH_2Br} \quad \text{or} \quad \underset{\text{(II.)}}{COPh\cdot CRR'\cdot CH_2\cdot CHBr\cdot CH_2\cdot OH}$$

bromohydrins obtained. Dimethylallylacetophenone in this way gives *ε-bromo-β-benzoyl-β-methylpentan-δ-ol*,

$$COPh\cdot CMe_2\cdot CH_2\cdot CH(OH)\cdot CH_2Br,$$

m. p. 106°.

Diethylallylacetophenone gives *ζ-bromo-γ-benzoyl-γ-ethylhexan-ε-ol*, $COPh\cdot CEt_2\cdot CH_2\cdot CH(OH)\cdot CH_2Br$, m. p. 84—88°.

Methylbenzylallylacetophenone gives *ε-bromo-β-benzoyl-β-benzylpentan-δ-ol*, $COPh\cdot CMeBz\cdot CH_2\cdot CH(OH)\cdot CH_2Br$.

Methylallylacetophenone under similar conditions gives a stable dibromo-derivative, *δε-dibromo-β-benzoylpentane*,

$$COPh\cdot CHMe\cdot CH_2\cdot CHBr\cdot CH_2Br,$$

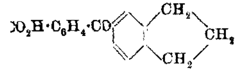
m. p. 128°. W. G.

Benzo-polymethylene Compounds. I. Certain Regularities in Substitution. JULIUS VON BRAUN, GEORG KIRSCHBAUM, and HANS SCHUHMANN (*Ber.*, 1920, **53**, [*B*], 1155—1173).—The communication is the first of a series devoted to the study of substances containing an aromatic nucleus to which a saturated hydrocarbon chain is cyclically attached. The action of oxalyl chloride, acetyl chloride, phthalic anhydride, and diethylmalonyl chloride on benzopentamethylene (hydrindene), tetrahydronaphthalene, and tetrahydroacenaphthene has been investigated. The behaviour of the first is not completely similar to that of either *o*-xylene or naphthalene; tetrahydronaphthalene, in contrast to naphthalene, yields only uniform products instead of mixtures of isomerides, whilst tetrahydroacenaphthene gives a mixture of monobasic acids with oxalyl chloride.

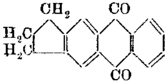
Hydrindene and oxalyl chloride react in carbon disulphide solution in the presence of aluminium chloride to yield mainly hydrindene-β-carboxylic acid, m. p. 178—179° (*chloride*, b. p. 140—142°/12 mm., *amide*, m. p. 137—138°), the constitution of which is deduced from its oxidation by nitric acid at 140° to trimellitic acid; hydrindene-α-carboxylic acid appears to be formed in small amount as by-product. Tetrahydronaphthalene and oxalyl chloride give exclusively tetrahydronaphthalene-β-carboxylic acid, b. p. 216°/14 mm., m. p. 152—153°, which is readily hydrogenated by sodium and amyl alcohol to decahydronaphthalene-β-carboxylic acid, b. p. 190—192°/21 mm., m. p. 79°. *Tetrahydronaphthalene-β-carboxylyl chloride* has b. p. 162°/13 mm., whilst the corresponding *amide* forms shining leaflets, m. p. 137—138°. Tetrahydroacenaphthene and oxalyl chloride yield a mixture of *acids*, which are separated by repeated crystallisation from alcohol; of these, the more sparingly soluble compound has m. p. 206° after softening at 200°, and is the main product. The isomeric acid has m. p. 170—180°, and has not been isolated in the pure state. Both isomerides yield benzene-1 : 2 : 3 : 4-tetracarboxylic acid when oxidised with nitric acid.

Acetyl chloride and hydrindene react readily, with formation of *β-hydrindyl methyl ketone*, b. p. 134—135°/11 mm. (*semicarb-*

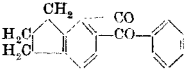
one, m. p. 229°, *oxime*, m. p. 114°; *β-hydrindyl bromomethyl* *tone*, leaflets, m. p. 58—59°, which do not attack the mucous embrane; *β-hydrindyl dibromomethyl ketone*, m. p. 58—59°). he *β*-position of the acetyl group follows from the oxidation of .e ketone by permanganate to hydrindene-*β*-carboxylic acid, and to an oily *acid*, which in all probability is *β*-hydrindoylformic acid, and is oxidised by nitric acid to trimellitic acid. Hydrindene and phthalic anhydride give exclusively



-hydrindoylbenzoic acid (annexed formula), m. p. 169°, which is onverted by zinc dust in ammoniacal solution into the *acid*, $H_2<^{CH_2}_{CH_2}>C_6H_3·CH_2·C_6H_4·CO_2H$, m. p. about 115°, but mainly nto the *lactone*, $CH_2<^{CH_2}_{CH_2}>C_6H_3·CH<^{C_6H_4}_{O}>CO$, m. p. 154°. t is decomposed with unusual difficulty by molten potassium ydroxide to yield hydrindene-*β*-carboxylic acid. When deydrated by fuming sulphuric acid, it gives a mixture of *ydrindanthraquinones*, delicate, matted needles, m. p. 180—181°, nd yellow, crystalline powder, m. p. 108—110°. The formulæ

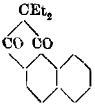


(I.)

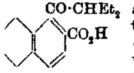


(II.)

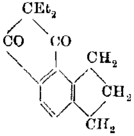
and II are assigned to these respectively, since the former, on reatment with zinc and ammonia, gives *hydrindanthracene*, m. p. 242—243°, whilst the latter only yields readily soluble products of lower melting point, from which a definite substance could not be isolated.



Tetrahydronaphthalene and diethylmalonyl chloride yield exclusively the *diethylindandione* derivative (annexed formula), b. p. 207—211°/ 15 mm., m. p. 56—57°, which is oxidised by nitric acid to benzene-1:2:3:4-tetracarboxylic acid, m. p. 238°. Concentrated potassium hydroxide solution transforms the liketone into an *acid*, m. p. 135°, which probably has the annexed constitution. Reduction of the diketone with amalgamated zinc and hydrochloric acid leads to the formation of the corresponding *hydrocarbon*, mobile oil, b. p. 164—166°/11 mm., which, however, is not completely free from oxygen; the latter can be totally eliminated by



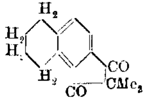
prolonging the duration of reduction, but, under these conditions, the hydrindene ring is ruptured, and the product is *γ-methyl-γ-*



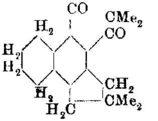
ethylbutyltetrahydronaphthalene, b. p. 141—144°/11 mm., which is oxidised by nitric acid to trimellitic acid. Diethylmalonyl chloride reacts with hydrindene in a precisely analogous manner, yielding the *product* (annexed formula), *pale yellow*, rather viscous oil, b. p. 186—191°/13 mm., which is oxidised by nitric acid to mellophanic acid, m. p. 238°. H. W.

Derivatives of *ac*-Tetrahydronaphthalene and of Tetrahydroacenaphthene. KARL FLEISCHER and FRITZ SIEFERT (*Ber.*, 1920, **53**, [*B*], 1255—1261).—The action of substituted malonyl chlorides on partly hydrogenated aromatic hydrocarbons has been investigated by Fleischer (*Zeitsch. angew. Chem.*, 1919, **32**, [ii], 596; 1920, **33**, [ii], 160). Since the same subject is also engaging the attention of von Braun (preceding abstract), the authors give an account of their work with *ac*-tetrahydronaphthalene and tetrahydroacenaphthene, but reserve the full experimental details for a later publication.

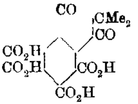
Dimethylmalonyl chloride and tetrahydronaphthalene yield exclusively 2 : 2-*dimethyltetrahydronaphth-αβ-indane*-1 : 3-*dione* (I), m. p. 75°, which is hydrolysed to 1-iso*butyryltetrahydro-*



(I.)

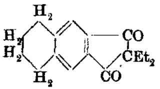


(II.)

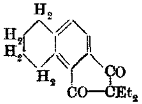


(III.)

naphthalene-2-carboxylic acid, m. p. 120°; the latter is oxidised by nitric acid to 2 : 2-dimethylbenzindane-1 : 3-dione-6 : 7-dicarboxylic acid. The indanedione is reduced by amalgamated zinc and hydrochloric acid to 2 : 2-*dimethyltetrahydronaphth-αβ-hydrindene*, b. p. 156°/18 mm. The αβ-position of the hydrindene ring in the hydrocarbon molecule is established by its conversion by dimethylmalonyl chloride into 2 : 2 : 5 : 5-*tetramethyltetrahydronaphthdihydrindane*-4 : 6-*dione* (II), m. p. 148—149°, which is reduced to 2 : 2 : 5 : 5-*tetramethyltetrahydronaphthdihydrindene*, *m. p.* 105—106°, and is oxidised by nitric acid to a tetracarboxylic acid (III), decomposing at 277°, and mellitic acid.



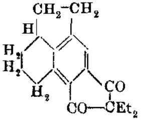
(IV.)



(V.)

With diethylmalonyl chloride and tetrahydronaphthalene, both isomerides are formed; 2 : 2-*diethyltetrahydronaphth-ββ-indane-1 : 3-dione* (IV) has m. p. 118°, whilst 2 : 2-*diethyltetrahydronaphth-αβ-indane*-1 : 3-*dione* (V) has m. p. 54—55°. Only the second of these yielded a well-defined *acid*, m. p. 134—135°, on hydrolysis. The former dione is oxidised by nitric acid to pyromellitic acid, whilst the latter gives 2 : 2-*diethylbenzindane*-1 : 3-*dione*-6 : 7-*dicarboxylic acid*, m. p. 174—176°. The diones are completely reduced by amalgamated zinc and hydrochloric acid to 2 : 2-*diethyltetrahydronaphth-ββ-hydrindene*, m. p. 49°, and 2 : 2-*diethyltetrahydronaphth-αβ-hydrindene*, b. p. 163—165°/12 mm., respectively.

[With Wilhelm Eckert.]—2-Acetyltetrahydronaphthalene is reduced to 2-*ethyltetrahydronaphthalene*, b. p. 127°/21 mm., from which, by regulated acetylation and subsequent reduction, 2 : 3-*diethyltetrahydronaphthalene*, b. p. 150—151°/18 mm., and 1 : 2 : 3-*triethyltetrahydronaphthalene*, b. p. 165—172°/23 mm., are successively prepared.



Tetrahydroacenaphthene is transformed by diethylmalonyl chloride into 2 : 2-*diethyltetrahydroacenaphth-αβ-indane*-1 : 3-*dione* (annexed formula), m. p. 88—89°, which is reduced by amalgamated zinc and hydrochloric acid to 2 : 2-*diethyltetrahydroacenaphth-αβ-hydrindene*, b. p. 190—195°/16 mm. The dione is oxidised to a mixture of benzenepentacarboxylic acid and *diethylbenzindane*-1 : 3-*dione*-4 : 5 : 6-*tricarboxylic acid*. H. W.

Menthol and Phenylhydrazine Derivatives of the Higher Fatty Acids. D. H. Brauns (*J. Amer. Chem. Soc.*, 1920, **42**, 1478—1481).—The menthyl esters and phenylhydrazine derivatives of certain of the higher fatty acids were prepared in an attempt to find a means of estimating the amounts of individual acids present in mixtures. This aim was not fulfilled. The menthyl esters prepared by heating the acid chlorides with menthol were *menthyl laurate*, D_4^{20} 0·8915, $[\alpha]_D^{20}$ −46·07°; menthyl myristate, m. p. 21—22°, D_4^{20} 0·882, $[\alpha]_D^{20}$ −42·33° (compare Hilditch, T., 1912, **101**, 192); menthyl palmitate, m. p. 32°, D_4^{20} 0·8848, $[\alpha]_D^{20}$ −39·10°; menthyl stearate, m. p. 38—39°, D_4^{45} 0·8665, $[\alpha]_D^{45}$ −36·60°; *menthyl arachidate*, m. p. 55°, D_4^{60} 0·8566, $[\alpha]_D^{60}$ −30·63°. All these rotations were determined directly on the molten substances. The phenylhydrazides, prepared by heating the acids with excess of phenylhydrazine, were *palmitic phenylhydrazide*, m. p. 105°; stearic phenylhydrazide, m. p. 110—111°; *arachidic phenylhydrazide*, m. p. 108—109°. W. G.

"Cresineol," a Compound of Cineole and *o*-Cresol. T. Tusting Cocking (*Pharm. J.*, 1920, **105**, 81).—When one molecule of cineole is mixed with one molecule of *o*-cresol, heat is developed, and a crystalline substance separates as the mixture

cools. The name "cresineol" is given to the substance. It has m. p. 55·2°, b. p. 186·5—189°, D_{60}^{60} 0·9661, and n_D^{60} 1·4846; it is soluble in most organic solvents, and is decomposed by alkali hydroxides into its constituents. W. P. S.

Dependence of Optical Rotatory Power on Chemical Constitution. II. The Effect of Position-isomerism and Conjugation on Optical Activity among Aryl Derivatives of Amino- and Bisimino-camphor. Bawa Kartar Singh, Dalip Singh, Guru Dutt, and Gopal Singh (T., 1920, **117**, 980—988).

Reduction Products of Hydroxymethylenecamphor. IV. Coupling of Bases with Methylenecamphor. Hans Rupe and Walter Kussmaul (*Helv. Chim. Acta*, 1920, **3**, 515—540. Compare A., 1919, i, 335).—Unsuccessful attempts have been made to prepare the methylcamphoramine of the structure,

$$C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot NH_2\\ |\\ CO\end{matrix},$$

(1) by treating camphylbromomethane with ammonia, and (2) by reduction of aminomethylenecamphor. Reaction (1) yields a compound which forms a nitrosoamine, a benzoyl derivative and a phenylthiocarbamide derivative, and may be obtained also by reduction with aluminium amalgam in neutral solution of the imide described by Bishop, Claisen, and Sinclair (A., 1895, i, 62); this compound is evidently di(camphomethyl)-amine,

$$C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot NH\cdot CH_2\cdot CH\\ |\qquad\qquad\qquad\quad |\\ CO\qquad\qquad\qquad\quad CO\end{matrix}>C_8H_{14}.$$

The latter is obtained also when methylenecamphor is treated with ammonia in a sealed tube, and when camphylcarbinol and ammonia react under pressure. Derivatives of the methylcamphoramine sought may, however, be obtained. Thus, the action of diethylamine on methylenecamphor gives diethylcamphomethylamine, $C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot NEt_2\\ |\\ CO\end{matrix}$, which is obtainable also from camphylbromomethane and diethylamine.

Reduction of aminomethylenecamphor by means of aluminium amalgam gives in small yield a base which is isomeric with, and exhibits quite similar behaviour to, the secondary base obtained by reaction (1), and is probably of the structure

$$C_8H_{14}<\begin{matrix}CMe\cdot NH\cdot CH_2\cdot CH\\ |\qquad\qquad\qquad |\\ CO\qquad\qquad\qquad CO\end{matrix}>C_8H_{14}.$$

Attempts were also made to prepare the desired methylcamphoramine by reducing methylenecamphoramide with hydrogen in presence of nickel, by means of camphylbromomethane and phthalimide, and from the amide of camphorylacetic acid (compare Rupe, Warder, and Takagi, A., 1919, i, 27), but in no case successfully.

Various quaternary ammonium compounds derived from methylene- and methyl-camphor are described. Noteworthy is the formation of the anhydride of hydroxymethylenecamphor (compare Bishop, Claisen, and Sinclair, *loc. cit.*) by treatment with sodium hydroxide of the quaternary base obtained from trimethylamine and methylenecamphor chloride:

$$C_8H_{14}<{C:CH\cdot NClMe_3 \atop CO} + H_2O = C_8H_{14}<{C:CH\cdot OH \atop CO} + NMe_3 + HCl \quad \text{and}$$

$$C_8H_{14}<{C:CH\cdot OH \atop CO} - H_2O = C_8H_{14}<{C:CH\cdot O\cdot CH:C \atop CO}\ {\atop CO}>C_8H_{14};$$

the trimethylamine liberated acts as the dehydrating agent.

Di(camphomethyl)-amine, $(C_{11}H_{17}O)_2NH$, forms an amorphous, crumbly, white mass of faintly basic odour, m. p. 124°, and decomposes on distillation even under reduced pressure. The *hydrobromide*, $(C_{11}H_{17}O)_2NH,HBr$, slender, white leaflets, sintering and blackening at 285°, and remaining unmelted at 350°; the *hydrochloride*, thin, white leaflets or felted needles with a persistent, bitter taste, sintering and blackening at 270°, and remaining unmelted at 350°; the *platinichloride*, quadratic leaflets, boiling suddenly and blackening at 240°; the *oxalate* (normal), microscopic, rectangular leaflets, decomposing at 191—192°; the *nitrosoamine*, $C_8H_{14}<{CH\cdot CH_2\cdot N(NO)\cdot CH_2\cdot CH \atop CO}\ {\atop CO}>C_8H_{14}$, slender, white needles, softening at 100°, m. p. 106°; and the *benzoyl* derivative, $C_{29}H_{39}O_3N$, bundles of slender needles, m. p. 132°, were prepared. *Di(camphomethyl)-phenylthiocarbamide*,

$$\left[C_8H_{14}<{CO \atop CH\cdot CH_2}\right]_2 N\cdot CS\cdot NHPh,$$

forms slender, silky needles, m. p. 160—161°, and is sometimes accompanied by an *isomeride*, m. p. 129—130°.

The *base*, $C_{22}H_{35}O_2N$, obtained by reducing aminomethylenecamphor by means of aluminium amalgam, forms a friable mass, softening at 130°, m. p. 145—146°. The following derivatives were prepared: *hydrochloride*, slender, rectangular leaflets, neither melting nor decomposing; *platinichloride*, decomposing at 230°; *oxalate*, glittering leaflets, softening at 250°, m. p. 258° (decomp.); *nitrosoamine*, $C_{22}H_{34}O_3N_2$, crystalline powder, softening at 158°, m. p. 164°.

Reduction of methylenecamphorimide by means of aluminium amalgam yields methylcamphor, di(camphomethyl)-amine, and a *base*, giving an oxalate, m. p. 248—250°.

Similar reduction of ethyl methylenecamphor-*p*-aminobenzoate yields ethyl *p*-aminobenzoate, together with a *compound*, $C_{20}H_{25}O_3N$ or $C_{20}H_{23}O_2N$, crystallising in small prisms, m. p. 278—279°.

Diethylcamphomethylamine, $C_{15}H_{27}ON$, is a pale yellow, oily liquid of faintly basic odour, b. p. 137·5°/8·5 mm. The *hydrochloride*, slender, white needles, m. p. 167—168·5°, giving a bitter,

aqueous solution, and the *platinichloride*, slender, salmon-coloured needles, m. p. 194°, decomposing at 212°, were prepared.

Methylenecamphortrimethylammonium chloride,

$$C_8H_{14}<\begin{matrix}C\colon CH\cdot NMe_3Cl\\ |\\ CO\end{matrix},$$

prepared from methylenecamphor chloride and trimethylamine, forms vitreous, quadratic, deliquescent plates, m. p. 162°, and yields intensely bitter, aqueous solutions. With sodium hydroxide, the aqueous solution of the chloride yields trimethylamine, and, on subsequent acidification, hydroxymethylenecamphor; when heated in a reflux apparatus on a boiling-water bath, it gives the anhydride of hydroxymethylenecamphor.

Methylcamphortrimethylammonium chloride could not be prepared, but the corresponding bromide, obtained from camphylbromomethane and trimethylamine, forms with trimethylamine hydrobromide the *compound*,

$$C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot NMe_3Br\\ |\\ CO\end{matrix}, 2NHMe_3Br,$$

which crystallises in colourless leaflets, softening at 183°, melting at 192°, again solidifying and melting a second time, and boiling at 286°. T. H. P.

Essential Oil of Mosta grosseserrata, Maxim. YOSHIATSU MURAYAMA (*J. Pharm. Soc. Japan*, 1920, 389—408. Compare Furukawa and Tomizawa, *J. Chem. Ind. Japan*, 1919, **22**, 383).—Three specimens of the essential oil from the wild plant contained: (1) thymol, methyleugenol, *p*-cymene, a terpene, and a sesquiterpene, b. p. 136°/12 mm.; (2) thymoquinol; (3) myristicin. The oil from the cultivated plant contained thymoquinol, thymol, and a terpene. K. K.

Hiptagin, a New Glucoside from Hiptage madablota, Gaertn. K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], **2**, 187—202).—This glucoside is extracted in a yield of 8% from the root bark by acetone or ethyl acetate. The bark of the stem contains much less. *Hiptagin*, $C_{10}H_{14}O_9N_2,\frac{1}{2}H_2O$, forms silky needles, m. p. 110°, $[\alpha]_D$ +3·5° in 5% acetone solution. The most characteristic chemical property is the formation by dilute alkali hydroxide, even in the cold, of ammonia and hydrocyanic acid. Dilute acids act quite differently, forming dextrose, and, at the same time, breaking down the genin in various ways; 5% aqueous sulphuric acid at 100° forms tartronic acid. Concentrated hydrochloric acid, mixed with 4 volumes of acetone, forms in five days at the ordinary temperature strong, monobasic *hiptagenic acid*, $C_3H_5O_4N$, needles, m. p. 68°, $k = 1{\cdot}20 \times 10^{-4}$, giving crystalline *silver*, *lead*, and *zinc* salts. The hypothetical hiptagenin is decomposed according to the equation $C_4H_4O_4N_2 + 2H_2O = C_3H_5O_4N + CO_2 + NH_3$. Hiptagenic acid is also formed by destructive distillation of the glucoside, and is regarded as having the constitution $OH\cdot NH\cdot CO\cdot C(OH)\colon CH\cdot OH$. By heating hiptagenic acid

with hydrochloric acid on the water-bath, it is hydrolysed to diglycollic and formic acids and to hydroxylamine hydrochloride, $2C_3H_5O_4N + 3H_2O = C_4H_6O_5 + 2HCO_2H + 2NH_2{\cdot}OH$. Sodium ethoxide at the ordinary temperature decomposes hiptagin, with the formation of sodium nitrite, but hiptagenic acid is only slowly hydrolysed by boiling alcoholic sodium ethoxide solution, probably with the formation of formhydroxamic acid (red coloration with ferric chloride) and of glyoxal, $OH{\cdot}CH{:}C(OH){\cdot}CO{\cdot}NH{\cdot}OH = OH{\cdot}CH{:}N{\cdot}OH + CHO{\cdot}CHO$. The action of aqueous alkalis on hiptagenic acid is very complex. The best results were obtained by heating with barium hydroxide at 50°, which formed barium nitrite, barium formhydroxamate, and (in 72% yield) a salt,

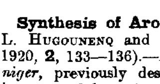
$$C_3H_3O_4NBa.$$

The latter is regarded as derived from a carbamic acid,

$$OH{\cdot}CH{:}C(OH){\cdot}NH{\cdot}CO_2H,$$

isomeric with hiptagenic acid. On heating with phosphoric acid, the barium salt gives half a molecular proportion of carbon dioxide, hydrocyanic and oxalic acids, ammonia, formaldehyde, and glyoxal. The isomerisation of hiptagenic to the carbamic acid is compared to the Beckmann transformation of oximes. The carbamic acid may be decomposed on the one hand to ammonia and glyoxal, and on the other to formaldehyde, water, and cyanoformic acid. The last-named may yield hydrocyanic acid and carbon dioxide, or oxalic acid and ammonia. Glyoxal and formaldehyde were obtained as *p*-nitrophenylhydrazones.

The action of barium hydroxide on hiptagin takes place according to the equation $C_{10}H_{14}O_9N_2 + 3H_2O = C_6H_{12}O_6 + C_3H_5O_4N + CO_2 + NH_3$. The barium salt of the carbamic acid here has the composition $(C_3H_4O_4N)_2Ba$, and appears to be derived from the tautomeric form,



$$CHO{\cdot}CH(OH){\cdot}NH{\cdot}CO_2H,$$

without the two acid hydroxymethylene groups formulated above for the salt from hiptagenic acid. The author proposes for hiptagin the annexed formula of an *iso*oxazole derivative. He considers that it is formed in the plant by reduction of nitrates to hydroxylamine, and condensation of this base with aldehydes and ketones. G. B.

Synthesis of Aromatic Amino-acids in the Living Cell. L. Hugounenq and Gabriel Florence (*Bull. Soc. chim. Biol.*, 1920, **2**, 133—136).—Aspergillin, the black pigment of *Aspergillus niger*, previously described by Linossier (A., 1891, 751, 1089), is prepared by extracting the spores with cold 10% sodium hydroxide. The extract, on being neutralised with sulphuric acid, produces a flocculent, black precipitate of the pigment in a more or less pure condition. After purification, the product forms a shining, amorphous powder, insoluble in water and in acids, but very soluble in alkalis. It contains 4·97% of ash, in which were present iron, sulphur, zinc, and calcium. Elementary analysis gave the percentage figures: C 43·5, H 6·9, N 12·6, P 8·7, Fe 0·455,

Ca 0·352, Mg 0·126, S 0·57, O 27·367. It appears to contain an indole ring in the molecule. J. C. D.

Henna (Lawsonia inermis). Chemical Constitution of Lawsone. II. G. TOMMASI (*Gazzetta*, 1920, **50**, i, 263—272).—Lawsone, the colouring matter contained in henna leaves (compare *Ann. R. Staz. Chim. agr. sper. Roma*, 1920, **10**), forms crystals, m. p. 192—195° (decomp.), and gives an orange-yellow, aqueous solution, which undergoes change when boiled. It is fixed well by wool and silk, and, rapidly and tenaciously, by the skin. In aqueous solutions of alkali or alkaline earth hydroxides, or in concentrated sulphuric acid, it dissolves, giving a bright orange-red coloration. In aqueous-alcoholic solution it gives: with ferric chloride, a reddish-brown precipitate; with stannous chloride or alum, a yellow precipitate; with copper acetate, an orange precipitate; with silver nitrate, an orange-red precipitate; with tannin it remains unchanged.

Its composition and its ebullioscopic behaviour in alcohol indicate the formula $C_{10}H_6O_3$, and it is distinctly acid in character and contains no methoxyl groups. The *calcium* salt, $Ca(C_{10}H_5O_3)_2$, forms silky, red needles. The *acetyl* derivative, $C_{10}H_5O_2{\cdot}OAc$, crystallises in shining needles, m. p. 128—130°. When reduced by means of zinc dust and acetic acid, it is converted into a colourless leuco-derivative, which is readily oxidised to the original compound by atmospheric oxygen. By treatment with acetic anhydride and zinc dust, it is transformed into the *compound*, $C_{16}H_{14}O_6$, which crystallises in nacreous, white laminæ, m. p. 133—134°. The conclusion is drawn that the molecule of lawsone contains one phenolic hydroxylic oxygen atom and two quinonic oxygen atoms. Further, since, in alcoholic solution, lawsone gives with nickel acetate an intense red coloration, and after some hours a deposit of garnet-red crystals (compare Brissemoret and Combes, A., 1907, ii, 411), the substance must be regarded as a hydroxynaphthaquinone, and is probably identical with 2-hydroxy-1:4-naphthaquinone. T. H. P.

Formation of Melanin. J. VERNE (*Compt. rend. Soc. Biol.*, 1920, **83**, 760—762; from *Chem. Zentr.*, 1920, iii, 156).—The brown dye, which has been proved histologically to be converted into melanin, is completely soluble in warm water, alkaline and acid solutions, and in formalin, but quite insoluble in alcohol and solvents for fats. The aqueous solution is faintly acidic, does not give the biuret or purine reactions, dissolves cupric hydroxide, and is readily diazotised. Addition of neutral formalin renders the solution strongly acidic. Addition of solutions of tyrosinase causes rapid blackening. Millon's reaction is strongly marked. The dye consists of polypeptides in which tyrosine is present, and is classed as an amino-acid dye. A considerable portion of the nitrogen, which can be titrated with formalin, disappears during the formation of melanin, whilst the total nitrogen remains unchanged. H. W.

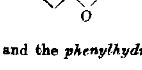
The Constitution of Catechin. I. MAXIMILIAN NIERENSTEIN (T., 1920, **117**, 971—979).

Syntheses in the Bergaptene Group. P. KARRER, A GLATTFELDER, and FR. WIDMER (*Helv. Chim. Acta*, 1920, **3**, 541—558).—Condensation of 5-hydroxy-2-methylcoumarone with hydrocyanic acid and hydrogen chloride yields 5-hydroxy-2-methylcoumarone-4-aldimide hydrochloride, and the latter, when boiled with water, yields an aldehyde which is to be investigated later, but is most probably 5-hydroxy-2-methylcoumarone-4-aldehyde. When heated with acetic anhydride and sodium acetate, this aldehyde yields an "intermediate compound," which is converted when boiled with distilled water into 5-hydroxy-2-methylcoumarone-4-acrylic acid; treatment of the latter with methyl sulphate in concentrated alkaline solution yields 5-methoxy-2-methylcoumarone-4-acrylic acid, whilst in faintly alkaline solution methyl 5-methoxy-2-methylcoumarone-4-acrylate is obtained. The acrylic acid is highly stable, and shows not the slightest tendency to undergo dehydration to the corresponding coumarin; similarly, 5-hydroxy-4-chloroacetyl-2-methylcoumarone exhibits no tendency to ring-formation with loss of hydrogen chloride, the phenomenon in both cases being probably due to steric hindrance.

In order to exclude the influence of the methyl group of the furan ring and to approach more closely to the natural products, bergaptene and xanthotoxin, coumarone–coumarin derivatives free from methyl groups have been prepared. 5-Hydroxycoumarone is obtainable with difficulty from 7-acetoxycoumarin (compare Pechmann, A., 1884, 1173) by way of the dibromide and 5-hydroxycoumarone-1-carboxylic acid. 5-Hydroxycoumarone reacts with hydrocyanic acid and hydrogen chloride, giving 5-hydroxycoumarone-4-aldimide hydrochloride, which is converted on hydrolysis with hot water into 5-hydroxycoumarone-4-aldehyde. Like the methylated compounds mentioned above, this aldehyde is not converted into the coumarin expected when boiled with acetic anhydride and sodium acetate.

The methyl ether of phloroglucinol undergoes condensation with ethyl acetoacetate and sodium, yielding an ethyl methoxyhydroxymethylcoumaronecarboxylate. Cautious sublimation of the corresponding free acid gives the methoxymethylcoumarone, in which the closure of the coumarone ring takes place in either the ortho- or the para-position to the methoxyl group of the benzene nucleus.

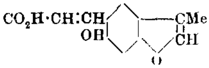
5-*Hydroxy-2-methylcoumarone-4-aldehyde* (annexed formula),



crystallises in pale yellow needles, m. p. 181°, and in alcoholic solution gives a green coloration with ferric chloride. The *oxime*, $C_{10}H_9O_3N$, forms long, white needles, m. p. 186° (decomp.), the *anil*, $C_{16}H_{13}O_2N$, yellow or yellowish-brown needles, m. p. 160° (decomp.), and the *phenylhydrazone*, yellow crystals, m. p. 165° (decomp.).

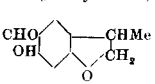
The intermediate *compound* (see above) forms small, yellow crystals, m. p. 114°, and is insoluble in sodium carbonate, hydrogen carbonate, or hydroxide solution.

5-*Hydroxy-2-methylcoumarone-4-acrylic acid* (annexed formula)



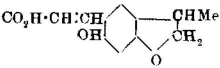
crystallises in shining, pale yellow needles, m. p. 199°, sublimes partly at a higher temperature, dissolves readily in alkali solutions, and in acetone solution decolorises permanganate. 5-*Methoxy-2-methylcoumarone-4-acrylic acid*, $C_{13}H_{12}O_4$, forms pale yellow needles, m. p. 209°, and dissolves readily in alkali solution. Its *methyl* ester, $C_{14}H_{14}O_4$, crystallises in yellow needles, m. p. 216°.

5-*Hydroxy-2-methylcoumaran-4-aldehyde* (annexed formula), pre-

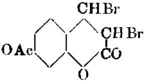


pared by the action of boiling water on the aldimide hydrochloride obtained by condensing 5-hydroxy-2-methylcoumaran (A., 1919, i, 595) with hydrocyanic acid and hydrogen chloride, crystallises in needles, m. p. 185°. The *oxime*, $C_{10}H_{11}O_3N$, m. p. 190° (decomp.), the *anil*, and the *hydrazone* were prepared.

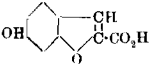
5-*Hydroxy-2-methylcoumaran-4-acrylic acid* (annexed formula),



prepared by boiling the preceding compound with acetic anhydride and sodium acetate, crystallises in pale yellow needles, m. p. 208°. In this case also no compound of coumarin character could be obtained.

7-*Acetoxycoumarin dibromide*,  , forms white leaflets, m. p. 114° (frothing).

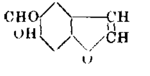
5-*Hydroxycoumarone-1-carboxylic acid* (5-*hydroxycoumarilic acid*) (annexed formula), prepared by the



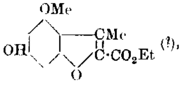
action of alcoholic potassium hydroxide on the preceding compound, crystallises in microscopic leaflets, m. p. 234—236° (uncorr.) (decomp.), gives a brown coloration in alcoholic solution with ferric chloride, and dissolves in aqueous alkali to a solution showing blue fluorescence, which disappears when the liquid is boiled.

5-*Hydroxycoumarone*, obtained by rapid distillation of 5-hydroxycoumarilic acid with calcium oxide, forms long, flat needles, m. p. 56°, dissolves readily in alkali solution, quickly decolorises permanganate in acetone solution, gives a green coloration in alcoholic solution with ferric chloride, and is resinified with a red coloration by concentrated sulphuric acid.

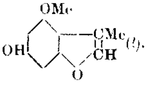
5-*Hydroxycoumarone-4-aldehyde* (annexed formula) forms white crystals, decomposes without melting at 260°, and in alcoholic solution gives a canary-yellow coloration with aniline hydrochloride. When boiled with acetic anhydride and sodium acetate it yields a compound which has not the composition of a simple coumarone–coumarin.



Ethyl hydroxymethoxymethylcoumaronecarboxylate (I), forms



(I.)

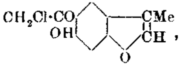


(II.)

crystals, m. p. 230°. The corresponding *acid* forms a white precipitate, m. p. 202° (decomp.).

Hydroxymethoxymethylcoumarone (II) is obtained as a white sublimate, m. p. 75° (previous softening), and has the odour of coumarone.

5-*Hydroxy-4-chloroacetyl-2-methylcoumarone*,



obtained from 5-hydroxy-2-methylcoumarone and chloroacetonitrile, forms crystals, m. p. 192°, and dissolves readily in dilute sodium hydroxide solution. T. H. P.

3 : 6-Tetramethyldiaminoselenopyronine. M. BATTEGAY and G. HUGEL (*Bull. Soc. chim.*, 1920, [iv], **27**, 557—560).—A mixture of sodium selenite and sulphuric acid is added gradually to sulphuric acid containing 25% of sulphur trioxide and at the same time tetramethyldiaminodiphenylmethane is added in small portions, so that it is always present in slight excess, the temperature not being allowed to rise above 35°. After an hour and a-half the mixture is poured on to ice, filtered, and a solution of zinc chloride added to the filtrate. The *zincichloride* of *tetramethyldiaminoselenopyronine*, $C_{17}H_{19}N_2Cl_3Se,ZnCl_2$, is obtained in a crystalline form. It dissolves in sulphuric acid to a red solution, which on dilution with water turns blue. The addition of sodium hydroxide to this solution precipitates a reddish-blue base, which is soluble in ether. The colouring matter gives slightly soluble iodides and nitrates and insoluble dichromates. W. G.

Synthesis of Derivatives of 1 : 3-Oxthiophan. A. BISTRZYCKI and BRUNO BRENKEN (*Helv. Chim. Acta*, 1920, **3**, 447—467).—The behaviour of thiobenzylic acid (α-mercaptodiphenylacetic acid) (com-

pare Becker and Bistrzycki, A., 1915, i, 245) towards aldehydes, ketones, and ketonic acids is found to be analogous to that of thioglycollic acid (Bongartz, A., 1886, 937; 1888, 478) and α-thiolactic acid (Holmberg and Mattisson, A., 1907, i, 475) towards these carbonylic compounds.

4:4-*Diphenyl*-1:3-*oxthiophan*-5-*one* (methylene ether ester of thiobenzylic acid), $CPh_2<\begin{array}{l}S-CH_2\\CO\cdot O\end{array}$, prepared by the interaction of formaldehyde and thiobenzylic acid, crystallises in flat prisms or rhombic or triangular plates, m. p. 99—100°. Alkali carbonate or hydroxide decomposes it with formation of thiobenzylic acid, whilst with ammonia solution it yields diphenylacetamide and diphenylacetic acid. It is not changed by concentrated hydrochloric acid at 100°, but dissolves gradually in concentrated sulphuric acid to a yellow solution, which becomes deep violet after a few minutes or more rapidly on heating. It is not attacked by bromine in boiling chloroform solution. By zinc dust and boiling acetic acid it is decomposed, yielding thioformaldehyde (?) and diphenylacetic acid, whilst chromic anhydride in acetic acid converts it into

4:4-*Diphenyl*-1:3-*oxthiophan*-5-*one*-3-*dioxide*, $CPh_2<\begin{array}{l}SO_2\cdot CH_2\\CO-O\end{array}$, which crystallises in glistening, quadrilateral leaflets or flat prisms, m. p. 92—94°, and with concentrated sulphuric acid yields a cupric blue solution deepening considerably in colour when heated. When a solution of the sulphone in dilute, boiling alkali hydroxide is rendered acid with hydrochloric acid, it yields sulphur dioxide and a white, flocculent precipitate.

4:4-*Diphenyl*-2-*methyl*-1:3-*oxthiophan*-5-*one*, $CPh_2<\begin{array}{l}S-CHMe\\CO\cdot O\end{array}$, prepared from acetaldehyde and thiobenzylic acid, forms microscopic, colourless, four-sided plates, often in bundles, m. p. 89—91°, and behaves towards concentrated sulphuric acid similarly to its lower homologue.

4:4-*Diphenyl*-2-*methyl*-1:3-*oxthiophan*-5-*one*-3-*dioxide*,

$$CPh_2<\begin{array}{l}SO_2\cdot CHMe\\CO-O\end{array},$$

obtained on oxidising the preceding compound, exists in two modifications, which are possibly stereoisomerides related in the manner indicated by Hinsberg (A., 1916, i, 725; 1917, ii, 173, 461). The *α-form* crystallises in colourless plates, m. p. 79—81°, and dissolves in hot concentrated sulphuric acid with formation of a reddish-brown solution with a violet reflexion. The *β-form*, obtained along with the α-form or by treating the latter with boiling acetic acid, crystallises in colourless, microscopic rhombohedra, m. p. 97—98°.

4:4-*Diphenyl*-2-*trichloromethyl*-1:3-*oxthiophan*-5-*one*,

$$CPh_2<\begin{array}{l}S-CH\cdot CCl_3\\CO\cdot O\end{array},$$

prepared from chloral and thiobenzylic acid, forms colourless, pris-

matic plates, m. p. 107°. In hot concentrated sulphuric acid it dissolves with emission of an intense garlic odour and formation of a violet solution, turning first blue and then an indistinct green.

2 : 4 : 4-*Triphenyl*-1 : 3-*oxthiophan*-5-*one*, $CPh_2<\begin{matrix}S-CHPh\\ CO\cdot O\end{matrix}$, obtained from benzaldehyde and thiobenzylic acid, forms colourless, mostly hexagonal plates, m. p. 94—96°. With ammonia solution at 125° it gives a small yield of a *compound*, m. p. 163—165°, of unknown character. It is not attacked by concentrated hydrochloric acid at 100°, but with aniline it furnishes an *additive compound*, $C_{21}H_{16}O_2S,NH_2Ph$, which crystallises in bundles of colourless plates, softening at 67°, then gradually melting and giving a clear liquid only at 77·5°. It is not changed at 100° by methyl iodide in presence or absence of methyl alcohol, but undergoes profound decomposition when boiled with a chloroform solution of bromine. With concentrated sulphuric acid it gives a yellow solution, quickly becoming violet-red with slight evolution of gas.

2 : 4 : 4-*Triphenyl*-1 : 3-*oxthiophan*-5-*one*-3-*oxide*, $CPh_2<\begin{matrix}SO-CHPh\\ CO\cdot O\end{matrix}$, obtained by oxidising the preceding compound, crystallises in microscopic prisms, often united in bundles, m. p. 158·5—160·5°, and in concentrated sulphuric acid yields a greenish-yellow solution becoming violet-brown when heated. When boiled with normal potassium hydroxide solution, it emits an odour of benzaldehyde.

4 : 4-*Diphenyl*-2-p-*chlorophenyl*-1 : 3-*oxthiophan*-5-*one*,

$$CPh_2<\begin{matrix}S-CH\cdot C_6H_4Cl\\ CO\cdot O\end{matrix},$$

obtained from *p*-chlorobenzaldehyde, crystallises in slender, silky prisms or concentric aggregates of colourless, four-sided prisms, m. p. 125—126°, and towards concentrated sulphuric acid behaves like the chlorine-free compound.

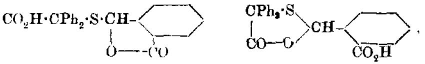
4 : 4-*Diphenyl*-2-o-*nitrophenyl*-1 : 3-*oxthiophan*-5-*one*, $C_{21}H_{15}O_4NS$, from *o*-nitrobenzaldehyde, forms colourless, four-sided plates, m. p. 116·5—117·5°, and gives a violet-brown solution in concentrated sulphuric acid.

4 : 4-*Diphenyl*-2-m-*nitrophenyl*-1 : 3-*oxthiophan*-5-*one*, $C_{21}H_{15}O_4NS$, from *m*-nitrobenzaldehyde, forms iridescent, white, quadrilateral plates, m. p. 132—133°.

4 : 4-*Diphenyl*-2-o-*hydroxyphenyl*-1 : 3-*oxthiophan*-5-*one*, $C_{21}H_{16}O_3S$, formed from salicylaldehyde, crystallises in colourless, microscopic rhombs, m. p. 147° (decomp.), and dissolves in concentrated sulphuric acid to a greenish-orange solution, becoming violet-brown when heated. In ammonia solution it gives a greenish-yellow solution, and in normal potassium hydroxide a greenish-brown solution which soon loses its colour. Its *acetyl* derivative, $C_{23}H_{18}O_4S$, forms flat prisms or concentric aggregates of microscopic, rhombic plates, m. p. 104—105°.

4 : 4-*Diphenyl-2-p-anisyl-1 : 3-oxathiophan-5-one*, $C_{22}H_{18}O_3S$, obtained from anisaldehyde, forms colourless, microscopic plates or heavy plates, m. p. 103—104°, and dissolves in concentrated sulphuric acid to a greenish-yellow solution, rapidly turning orange-brown.

The γ-*lactone* (I), or, possibly, (II), obtained from *o*-phthalalde-



(I.) (II.)

hydic acid and thiobenzylic acid, crystallises in microscopic, four-sided plates, turns blue at 150°, and decomposes at 168°; it forms also the hydrate, $+H_2O$, which softens at 115°. It dissolves in concentrated sulphuric acid, giving a yellowish-brown solution, quickly turning brownish-red with a violet tinge. Its *barium* salt was prepared and analysed.

4 : 4-*Diphenyl-2-styryl-1 : 3-oxthiophan-5-one*,

$CPh_2{\cdot}S\!\!>\!\!CH{\cdot}CH{:}CHPh$, over $CO{-}O$,

obtained from cinnamaldehyde, forms microscopic, colourless, pointed, rhombic plates, m. p. 156—157° (decomp.); its solution in concentrated sulphuric acid is orange-coloured, and slowly becomes brown or, when heated, brownish-red.

4 : 4-*Diphenyl-2 : 2-dimethyl-1 : 3-oxthiophan-5-one*, $CPh_2{\cdot}S$/$CO{-}O$ $>CMe_2$, obtained from acetone and thiobenzylic acid, forms flat, white prisms, m. p. 119·5—120·5°, gives a brownish-red solution with a violet tinge in concentrated sulphuric acid, and is decomposed into its components when boiled with alcoholic potassium hydroxide solution.

2-*Carboxy-4 : 4-diphenyl-2-methyl-1 : 3-oxthiophan-5-one*,

$CPh_2{\cdot}S$/$CO{-}O$ $>CMe{\cdot}CO_2H$,

obtained from methylsuccinic acid and thiobenzylic acid, crystallises in truncated, double pyramids or microscopic, colourless, four-sided plates, softening at 156°, m. p. 160·5—162°. Towards concentrated sulphuric acid it behaves like the preceding compound. Its *silver* and *barium* salts form amorphous, white precipitates and rapidly decompose.

4 : 4-*Diphenyl-2-methyl-2-carbethoxymethyl-1 : 3-oxthiophan-5-one*, $CPh_2{\cdot}S$/$CO{-}O$ $>CMe{\cdot}CH_2{\cdot}CO_2Et$, formed from ethyl acetoacetate and thiobenzylic acid, crystallises in drusy aggregates of colourless, four-sided prisms, m. p. 65—66·5°, and dissolves in alkali hydroxide solution and, with an orange coloration, in concentrated sulphuric acid.

Ethylxanthodiphenylacetic acid, $OEt{\cdot}CS{\cdot}S{\cdot}CPh_2{\cdot}CO_2H$, obtained as sodium salt by the interaction of chlorodiphenylacetic acid and

potassium xanthate in presence of sodium carbonate, forms bundles of shining, colourless prisms, sintering slightly at 140°, m. p. about 167°. Its solution in concentrated sulphuric acid is bright red with a violet tinge, and becomes turbid and orange-brown when heated. The *barium* salt was prepared and analysed. Unsuccessful attempts were made to decompose the acid with formation of thiobenzylic acid.

Improved yields of thiobenzylic acid may be obtained by a modification of Becker and Bistrzycki's method (A., 1915, i. 245). The product given by Bettschart and Bistrzycki's method, which involves the use of the additive compound of benzylic acid and allylthiocarbimide (A., 1919, i, 207), is less pure than that obtained with the help of phenylthiocarbimide.

Coupling of thiobenzylic acid with acetophenone, benzophenone, dibenzyl ketone and benzil could not be effected. T. H. P.

Syntheses in the Cinchona Series. IV. Nitro- and Amino-derivatives of the Dihydro-alkaloids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1920, **42**, 1481—1489).—Using the methods described (compare D.R.-P. 283537), it was found that satisfactory results were not obtained in the preparation of 5-nitro- and 5-amino-dihydroquinine. During the nitration of dihydroquinine, sulphonation also occurred, and a nitrosulphonic acid was obtained. By nitration in fuming nitric acid (D 1·52), however, without the addition of sulphuric acid, an excellent yield of 5-nitrodihydroquinine, m. p. 220—222°, $[\alpha]_D^{25}$ −200·0° (in chloroform), was obtained. 5-*Nitrodihydroquininesulphonic acid*, m. p. 260—285° (decomp.), $[\alpha]_D^{25}$ −133·0° (in *N*/2-sodium hydroxide), was obtained either by nitration of dihydroquininesulphonic acid or by sulphonation of 5-nitrodihydroquinine.

5-Nitrodihydroquinine is best reduced by adding it slowly, with stirring, to cold, concentrated hydrochloric acid until it is all dissolved, and then adding stannous chloride to the solution at 0°, the temperature not being allowed to rise above 35°. The base was finally obtained in yellow needles, m. p. 220—221°, $[\alpha]_D^{21}$ −17·7°.

These methods were successfully used for the preparation of nitro- and amino-derivatives from other dihydro-alkaloids of this series, the following compounds being obtained.

5-*Nitroethyldihydrocupreine* (5-*nitro-optochin*), m. p. 225—226° (decomp.), $[\alpha]_D^{22.5}$ −198·2° (in chloroform); 5-aminoethyldihydrocupreine, m. p. 214—215° (decomp.), $[\alpha]_D^{24.5}$ −15·9° (in alcohol) (compare Giemsa and Halberkann, A., 1919, i, 342).

5-*Nitrodihydroquinidine*, m. p. 208—209°, $[\alpha]_D^{23}$ +326·5° (in alcohol), which gives a *nitrate*, $C_{20}H_{25}O_4N_3,HNO_3$, $[\alpha]_D^{25}$ +232·8°; 5-*aminodihydroquinidine*, m. p. 235°, $[\alpha]_D^{20}$ +115·5° (in alcohol).

5-*Nitroethyldihydrocupreidine*, m. p. 220—221° (decomp.), $[\alpha]_D^{23}$ +322·4° (in alcohol); 5-*aminoethyldihydrocupreidine*, m. p. 216—217°, $[\alpha]_D^{26.5}$ −69·4° (in chloroform), +91·6° (in alcohol).

5-*Nitrodihydrodeoxyquinine*, $C_{20}H_{25}O_3N_3,3\frac{1}{2}H_2O$, m. p. 67·5—69°, $[\alpha]_D^{22}$ +80·2° (in alcohol). Attempts to reduce this compound were not successful. W. G.

Syntheses in the Cinchona Series. V. Dihydrodeoxyquinine and Dihydrodeoxyquinidine and their Derivatives. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1920, **42**, 1489—1502. Compare preceding abstract).—The series of compounds studied consisted of dihydroquinine ⟶ chlorodihydroquinine ⟶ dihydrodeoxyquinine ⟶ dihydrodeoxycupreine ⟶ ethyldihydrocupreine, and the similar series of quinidine derivatives, the methods of preparation employed being essentially those used by Koenigs (compare *Ber.*, 1895, **28**, 3147; 1896, **29**, 372) and Rabe (compare A., 1910, i, 417) for the non-hydrogenated derivatives.

Dihydroquinine dihydrochloride when acted on by phosphorus pentachloride gives *chlorodihydroquinine*, m. p. 143—144°, $[\alpha]_D^{21·5}$ +42·1° (in alcohol), giving a *hydrochloride*, m. p. 232—233° (decomp.) $[\alpha]_D^{20·5}$ −2·9°, and on reduction *dihydrodeoxyquinine*, $C_{20}H_{26}ON_2$, an oil, which yields a crystalline *trihydrate*, $[\alpha]_D^{21}$ −77·5° (in alcohol), a *picrate*, a *hydrochloride*, m. p. 179—180°, $[\alpha]_D^{22·5}$ −6·8°, a *dihydrochloride*, and a *methiodide*, $[\alpha]_D^{21}$ −7·4° (in alcohol). When demethylated by boiling with hydrobromic acid, dihydroquinine trihydrate yields *dihydrodeoxycupreine*, m. p. 191—191·5°, $[\alpha]_D^{22}$ −77·1° (in alcohol), giving a *hydrochloride*, m. p. 210°, $[\alpha]_D^{23}$ +1·5°, a *dihydrobromide*, m. p. 225—227°, a *methiodide*, m. p. 165—167°, $[\alpha]_D^{22}$ −37·6° and *ethyldihydrodeoxycupreine hydrochloride*, m. p. 185—186°, $[\alpha]_D^{23}$ −9·0°. When chlorodihydroquinine is demethylated by hydrobromic acid it yields *bromodihydrocupreine dihydrobromide*, m. p. 196—197°, $[\alpha]_D^{24}$ −69·1°.

Chlorodihydroquinidine, m. p. 93·5—95°, $[\alpha]_D^{22}$ +20·0° (in alcohol), gives a *hydrochloride*, m. p. 208—209°, $[\alpha]_D^{23}$ +39·7°, and on reduction yields *dihydrodeoxyquinidine dihydrate*, m. p. 81—83°, $[\alpha]_D^{22·5}$ +167·3° (in alcohol), giving a *picrate*, a *hydrobromide*, m. p. 151—152°, $[\alpha]_D^{24}$ +64·5°; a *dihydrobromide*, m. p. 225°, and a *methiodide*, m. p. 163—164°. When demethylated, dihydrodeoxyquinidine yields *dihydrocupreidine*, m. p. 183—183·5°, $[\alpha]_D^{24}$ +183·7°, giving a *hydrochloride*, $[\alpha]_D^{22}$ +76·8°, a *dihydrobromide*, and a *methiodide*, $[\alpha]_D^{23}$ +95·0°. *Bromodihydrocupreidine dihydrobromide* has $[\alpha]_D^{24}$ −47·7°.

Chloroquinidine gives a *hydrochloride*, m. p. 199—206° (decomp.), $[\alpha]_D^{23}$ +47·7°; deoxyquinidine gives a *hydrochloride*, m. p. 125°, $[\alpha]_D^{30}$ +81·9°; quinene gives a *dihydrochloride*, m. p. 110—185°, $[\alpha]_D^{24·5}$ +18·4°.

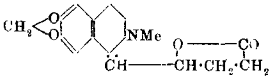
The authors suggest that in place of the prefix "deoxy" (desoxy) the suffix "ane" should be used, *e.g.*, in place of deoxyquinine they would use quinane. W. G.

Constitution of Lycorine [= Narcissine]. K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], **2**, 1—7. Compare A., this vol., i, 467).—Lycorine was obtained from the bulbs of *Crinum*

giganteum in a yield of 0·1—0·18% of the fresh material. Ewins' (narcissine) formula, $C_{16}H_{17}O_4N$ (T., 1910, **97**, 2406), was confirmed; $[\alpha]_D^{?}$ −120°. The hydrochloride, m. p. 206°, is soluble in twenty parts of water at 26°. The mercurichloride, the picrate, and the perchlorate decompose, respectively, at 149°, 196°, and 230°. Asahina and Sugii (A., 1913, i, 1093) found that lycorine when heated with phloroglucinol and sulphuric acid gives a reddish brown precipitate, indicating the presence of a methylenedioxy-group, already surmised by Ewins. Gorter has applied this reaction quantitatively by heating lycorine on the water-bath with 30% sulphuric acid, with and without resorcinol; the difference between the weight of the two precipitates corresponds roughly with that calculated for formalresorcinol from one methylenedioxy-group.

The above facts, and the blue fluorescence produced on adding a few drops of permanganate to lycorine sulphate solution, suggested a relationship to hydrastine, further emphasised by the opposite sign of the specific rotations of the free base (−120°) and of the hydrochloride (+43°).

With hydrogen and palladous chloride, lycorine is reduced to *dihydrolycorine*, $C_{16}H_{19}O_4N$, prisms, m. p. 247°, yielding a sparingly soluble *nitrate*, m. p. 243°. The reduced base is not made fluorescent by permanganate, whence the author concludes that the hydroxyl of the supposed lactonic side-chain is not adjacent to the *iso*quinoline nucleus, as in hydrastine, but rather that the fluorescence of lycorine is due to a double linking adjacent to this nucleus. Oxidation of lycorine with permanganate gave a small quantity of hydrastic and of oxalic acids, but no succinic acid, which leads the author to choose the annexed among various possible formulæ. G. B.



Ortho-para-isomerism in the Preparation of Diaminodiphenylmethane. Harold King (T., 1920, **117**, 988—992).

Manufacture of Asymmetric Carbamides. Axel Viggo Blom (Brit. Pat. 125584).—Asymmetric carbamides are produced by the action of the calculated quantity of carbonyl chloride on equimolecular proportions of an aminonaphtholsulphonic acid and a primary aromatic diamine in which the two amino-groups have different reaction speeds, in consequence of the presence of an ortho-substituent, as in the tolylenediamines, or of the substitution of one hydrogen atom by a formyl group. The operation must be conducted in such a way that the components are continuously brought into reaction in molecular proportions in a large vat, with efficient stirring, at a temperature of about 40° while a solution of an alkali hydroxide is run in in sufficient quantity just to neutralise the hydrogen chloride liberated. G. F. M.

Preparation of Derivatives of *p*-Nitrophenylcarbamide. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 319970 from *Chem. Zentr.*, 1920, iv, 132—133).—*p*-Nitrophenylcarbamide chloride is caused to react with primary or secondary bases or their substitution products, particularly sulphonic acids, hydroxysulphonic acid, etc., with or without reagents which absorb hydrogen chloride. The greenish-yellow lake-dye, pp′-*dinitrodiphenylcarbamide*, is obtained by heating *p*-nitrophenylcarbamide chloride with *p*-nitroaniline and nitrobenzene, or by the direct action of carbonyl chloride (1 mol.) on *p*-nitroaniline (2 mols.) if the initial temperature is not too high. Sodium sulphanilate and *p*-nitrophenylcarbamide chloride react in the presence of water and sodium acetate to yield *sodium* pp′-*nitrodiphenylcarbamidesulphonate*, yellow, crystalline powder, sparingly soluble in water, which is reduced by sodium sulphide solution to the corresponding colourless, more readily soluble *amino*-compound. The dark yellow *sodium ethylenebis*-pp′-*nitrodiphenylcarbamidesulphonate* is prepared from sodium *pp*′-diaminostilbenesulphonate. H. W.

Degradation Experiments with Dibromomaleic and Chlorofumaric Acids. PAUL RUGGLI and CARL HARTMANN (*Helv. Chim. Acta*, 1920, **3**, 493—514).—The authors have subjected dibromomaleic acid to those reactions which, as a rule, convert an acid into an amine with one carbon atom less than the acid, the object being to obtain the brominated amine, $NH_2 \cdot CBr{:}CBr \cdot NH_2$.

Ethyl dibromomaleate (compare Michael, A., 1893, i, 144; Pum, A., 1888, 1058; Ruhemann and Cunnington, T., 1899, **75**, 962) may be prepared by heating an alcoholic solution of dibromomaleic anhydride and hydrogen chloride under pressure. Attempts to obtain ditertiary glycols, and hence, by loss of water, dihydrofuran derivatives, by treating ethyl dibromomaleate with organomagnesium compounds, yielded unsatisfactory results. Ethyl hydrogen dibromomaleate, $CO_2H \cdot CBr{:}CBr \cdot CO_2Et$, crystallises in pale yellow, radiating needles, m. p. 65—67°; Salmony and Simonis gave m. p. 100°, which is erroneous (A., 1905, i, 631).

Dibromomaleic diamide, $NH_2 \cdot CO \cdot CBr{:}CBr \cdot CO \cdot NH_2$, forms slender, colourless needles, turns brown at 120°, and decomposes with evolution of bromine at 200°. Treatment of the diamide with bromine in a sealed tube at 90° yields dibromomaleimide, m. p. 227° (compare Dunlap, A., 1896, i, 471).

The *hydrazine* salt of *dibromomaleichydrazidic acid*,

$$NH_2 \cdot NH \cdot CO \cdot CBr{:}CBr \cdot CO_2H,N_2H_4,$$

forms slender, white needles, m. p. about 130° (decomp.), and in aqueous solution reacts with ammoniacal silver solution in the cold, whilst with neutral silver nitrate, silver dibromomaleate is precipitated. By dilute sulphuric acid, hydrazine sulphate is precipitated, and the action of benzaldehyde precipitates both the hydrazine molecules as benzylideneazine. By prolonged boiling

with dibromomaleic anhydride in alcoholic solution, the salt is converted quantitatively into the ammonium salt of

Dibromomaleic hydrazide [4 : 5-*dibromo*-3 : 6-*diketo*-1 : 2 : 3 : 6-*tetrahydropyridazine*], $CBr\lessdot\genfrac{}{}{0pt}{}{CO\cdot NH}{CBr\cdot CO}\gtrdot NH$, which forms yellow needles and is a highly stable compound; when slowly heated to above 300°, it gradually turns brown and decomposes, and when immersed in a bath at 340° it melts and decomposes. The *ammonium* salt, $C_4H_2O_2N_2Br_2\cdot NH_3$, forms almost colourless crystals, and does not reduce ammoniacal silver solution. The two *silver* salts, $C_4HO_2N_2Br_2Ag$ and $C_4O_2N_2Br_2Ag_2$, the *barium* salt ($+6H_2O$), and other salts have been prepared.

4 : 5-*Dibromo*-3-*ethoxy*-6-*keto*-1 : 6-*dihydropyridazine*,

$$CBr\lessdot\genfrac{}{}{0pt}{}{C(OEt):N}{CBr\text{---}CO}\gtrdot NH,$$

obtained by heating the di-silver salt of the preceding compound with ethyl iodide and alcohol, crystallises in white leaflets, m. p. 206°; its *silver* salt was prepared, but not in a pure state.

4 : 5-*Dibromo*-3-*acetoxy*-6-*keto*-1 : 6-*dihydropyridazine*,

$$CBr\lessdot\genfrac{}{}{0pt}{}{C(OAc):N}{CBr\text{---}CO}\gtrdot NH,$$

forms crystals, sintering at 225°, m. p. 228°, and has the normal molecular weight in boiling alcohol.

Ethylenediamine dibromomaleate, $C_4H_2O_4Br_2,C_2H_8N_2$, forms slender, white needles, turning brown at about 170°, and then decomposing.

Dibromomaleicdihydroxamic acid,

$$NOH:C(OH)\cdot CBr:CBr\cdot C(OH):NOH,$$

forms a hygroscopic, non-crystallisable mass; the *sodium* salt, $C_4H_2O_4N_2Br_2Na_2$, is also hygroscopic.

Chlorofumaric chloride, $COCl\cdot CCl:CH\cdot COCl$, prepared from tartaric acid and phosphorus pentachloride (compare Perkin, T., 1888, **53**, 696), may be freed from chlorides of phosphorus by shaking with water, if care be taken that no heating occurs. The diethyl ester of chlorofumaric acid, prepared by dropping alcohol on to the crude chloride (compare Claus, A., 1878, 855), gives vapour which strongly attacks the eyes.

Ethyl pyrazolone-3-carboxylate, $\genfrac{}{}{0pt}{}{CO\cdot CH_2}{NH\text{---}N}\gtrdot C\cdot CO_2Et$ (compare Rothenburg, A., 1893, i, 180, 367, 730; Ruhemann, T., 1896, **69**, 1394), prepared by the interaction of ethyl chlorofumarate and hydrazine hydrate, forms crystals, m. p. 178°, and with fuming nitric acid yields a violet solution giving, on neutralisation, a violet *compound*, m. p. 164°.

Bismonochlorofumarylhydrazine, $(CO_2H\cdot CH:CCl\cdot CO\cdot NH\cdot)_2$, obtained as hydrazine salt by the interaction of chlorofumaric chloride and hydrazine hydrate, forms almost colourless crystals, m. p. above 360°, and reduces ammoniacal silver solution in the

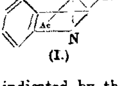
hot, but not Fehling's solution; it dissolves only in alkali solutions, giving deep yellow colorations. The *hydrazine* salt,

$$C_8H_{14}O_6N_6Cl_2,2H_2O,$$

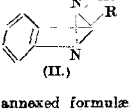
forms somewhat unstable, deep yellow crystals, m. p. 218°, and reduces Fehling's solution and ammoniacal silver solution immediately. T. H. P.

Structure- and Stereo-isomerism of Indazole Derivatives and the Constitution of Indazole. KARL VON AUWERS and MARIANNE DÜESBERG (*Ber.*, 1920, **53**, [*B*], 1179—1210).—Further details of the preparation and properties of the 1- and 2-alkyl-indazoles are recorded (compare A., 1919, i, 455), and the corresponding quaternary salts have been fully investigated. It is shown that the 2-alkyl derivatives, like the 1-alkyl compounds, have the power of uniting with one molecular proportion of alkali iodide, but that a second proportion cannot be added, although the quaternary iodide still contains a tertiary nitrogen atom. Identical products are obtained by the action of the isomeric 1- and 2-alkyl-indazoles on the iodide of the same alkyl, but isomeric quaternary compounds result from the interaction of alkylindazoles with the iodide of a different alkyl radicle. Homologous alkylindazoles of the same series give different additive products with reciprocal homologous alkyl iodides, whilst homologous alkylindazoles of different series give identical results when similarly treated. The quaternary iodides liberate alkyl iodide when heated above their melting points. The 1-alkyl derivatives eliminate the added alkyl iodide, and thus re-form the parent substance; on the other hand, the 2-alkyl compounds lose the alkyl group of the base in the form of alkyl iodide, and retain the radicle of the iodide used, or, in other words, the product of fission is a 1-alkyl derivative. The observations are most readily explained by assuming the general structure $C_6H_4<^{CH}_{NR'}>N<^{R}_{I}$, for the quaternary iodides. A method of converting 2-alkylindazoles into 1-derivatives is thus given, and also the simplest and best method of preparing the latter in the pure state.

Further instances of stereoisomerism among acylindazoles are recorded, and more definite evidence is adduced that the observed phenomena are actually due to stereoisomerism. The capability to yield such stereoisomerides disappears when an alkyl group is introduced into the 3-position. Apparently the possibility of stereoisomerism depends on the presence of a tervalent nitrogen atom in the ring, as



(I.)



(II.)

indicated by the annexed formulæ, and the phenomena are thus similar to those recently observed by Freund and Kessler and by Hess. The apparent disappearance of stereoisomerism in the cases of the alkyl derivatives finds its parallel in the frequent formation

ɔf stereoisomeric aldoximes and the infrequent occurrence of somerides of the type of acetophenoneoxime.

The authors have attempted to bring all available chemical and ɔhysical evidence to bear on the problem of the elucidation of the constitution of indazole itself. They are led to the conclusion that this cannot at present be conclusively settled, but that the balance of the evidence is greatly in favour of formula I rather than II.

$$C_6H_4\Big\langle{CH \atop N}\Big\rangle NH \qquad\qquad C_6H_4\Big\langle{CH \atop NH}\Big\rangle N$$

(I.) (II.)

2-Methylindazole, prisms or plates, m. p. 56°, b. p. 261°/ordinary ɔressure, 135°/16 mm., is prepared from methyl iodide and ndazole, from silver indazole and methyl iodide, and from 2-methylindazole-3-carboxylic acid at 230°; when crystallised from vater, it appears to form a monohydrate (compare Schad, A., 893, i, 280). It forms crystalline double *compounds* with silver iitrate and mercuric chloride. The *picrate* forms yellow, silky ɩeedles, m. p. 168°. 1-Methylindazole, m. p. 60—61°, b. p. 231°/ ordinary pressure, 109°/17 mm., is prepared from 1-methylindazole-3-carboxylic acid, or by the alkylation of indazole with methyl odide and sodium methoxide; the mixture of the 1- and 2-methyl lerivatives obtained by the latter method is separable by fractional listillation under ordinary or diminished pressure, or by crystalisation of the picrates. 1-*Methylindazole picrate* forms slender, ellow needles or coarse, transparent crystals, m. p. 136—137°. -Methylindazole yields crystalline double *compounds* with iercuric chloride and silver nitrate. 1:2-*Dimethylindazolium* ɔdide, m. p. 187°, is prepared by heating either 1- or 2-methylndazole with an excess of methyl iodide at 100°; the correspondng *picrate* has m. p. 167—168°. 2-*Ethylindazole* is a pale yellow il, b. p. 268°/ordinary pressure, 140°/14 mm.; the *picrate*, m. p. 55—156°, is immediately precipitated from dilute ethereal soluion in the form of slender needles, which are gradually transormed into coarse, transparent crystals. 1-*Ethylindazole* is a olourless oil, b. p. 126—127°/21 mm. (*picrate*, thin, pale yellow eedles, m. p. 148—150°). The action of ethyl iodide on 1-methylndazole or of methyl iodide on 2-ethylindazole at 100° leads to he production of 1-*methyl*-2-*ethylindazolium iodide*, small, olourless needles, m. p. 172·5—173° (*picrate*, m. p. 196—197°). -*Methyl*-1-*ethylindazolium iodide*, m. p. 154°, is similarly preared from 2-methylindazole and ethyl iodide or 1-ethylindazole ud methyl iodide; the corresponding *picrate* has m. p. 149—150°. :2-*Diethylindazolium iodide* forms coarse, colourless crystals, ı. p. 134° (*picrate*, m. p. 153°). 2:3-Dimethylindazole, m. p. 9—80°, yields a *picrate*, m. p. 224—225°, and is converted by ıethyl iodide into 1:2:3-*trimethylindazolium iodide*, colourless, lky needles, m. p. 220—221°. Decomposition by heat proceeds ormally in the cases of 1:2-dimethylindazolium iodide, 2-methyl-ethylindazolium iodide, and 1:2:3-trimethylindazolium iodide,

the product in the latter case being the 1:3-dimethyl derivativ 1-Methyl-2-ethylindazolium iodide yielded a mixture of 1-methy indazole (at least 75%) and 2-ethylindazole.

The stable form of 2-acetylindazole yields a crystalline *hydrochloride*, which is decomposed by exposure to moist air. The labil variety is completely transformed into the stable isomeride whe heated for thirty minutes at 100°. The additive compound c the labile form and mercuric chloride has m. p. 174—175° Hydrogen chloride decomposes the labile variety, with formatio of indazole hydrochloride. Stable *2-propionylindazole*, fror indazole and propionic anhydride at the ordinary temperature, ha b. p. 267°, m. p. 52°; it appears to be dimorphous. The labil *propionate* (from the silver salt or by the pyridine method) form pearly leaflets or shining, rhombic plates, m. p. 100·5—101·5°; i has b. p. 267°, and is then quantitatively converted into the stabl variety. The stable *benzoate* crystallises in slender, colourles needles, m. p. 94—95°. The labile *isomeride* forms small, coarse colourless crystals, m. p. 78°; it can be distilled without decom position at the ordinary pressure, and is thereby converted int the stable variety; the same change occurs slowly at the ordinar temperature, rapidly at 100°. Attempts to acetylate 3-methyl indazole by methods similar to those outlined above in connexio with the propionyl derivative led only to the formation of 2-acetyl 3-methylindazole, m. p. 72—73°. Similarly, only one form o *2-acetyl-3-ethylindazole*, slender prisms or large, well-define crystals, m. p. 35·5—36·5°, could be prepared from 3-ethyl indazole.

o-Nitrobenzoyl chloride is conveniently prepared by the actio of thionyl chloride on *o*-nitrobenzoic acid, and is converted by ethyl methylacetoacetate and sodium into *ethyl o-nitrobenzoyl methylacetoacetate*, which is hydrolysed by sulphuric acid (1:1) to *o-nitropropiophenone*, pale yellow, viscous, odourless oil, b. p 166—167°/15 mm., 161°/10—11 mm. (*semicarbazone*, m. p 182—183°); it is reduced by a large excess of stannous chloride to *o-aminopropiophenone*, pale yellow leaflets or hexagonal platelets m. p. 46—47° (*oxime*, needles, m. p. 88—89°). The aminoketone is converted according to the method of Fischer and Tafel int *3-ethylindazole*, slender, interwoven needles or coarse prisms m. p. 74·5—75·5°, b. p. 290°/atmospheric pressure, 157—158°/ 15 mm. The *picrate* has m. p. 152·5—153·5°. *2:3-Diethylindazole*, from 3-ethylindazole and ethyl iodide at 200°, is a colour less oil, b. p. about 287—290°, which does not show any tendency to crystallise; the *picrate* forms pale yellow needles, m. p 184—186° after previous softening. H. W.

Stereoisomeric Acyl Derivatives of Substituted Indazoles K. von Auwers and K. Schwegler (*Ber.*, 1920, **53**, [*B*] 1211—1232).—It has been shown previously (preceding abstract) that 2-acyl derivatives of indazole exist in two stereoisomeric forms of differing stability, whilst similar instances of stereo-

isomerism have not up to the present been observed with derivatives of the 3-alkylindazoles. The present communication deals with the effect of the entrance of substituents in the benzene nucleus. In every case which has been investigated, it has been found possible to isolate stereoisomeric acyl derivatives. The stability of the labile isomerides varies very greatly; in some instances the substances cannot be preserved unchanged for more than a few minutes, even at the ordinary temperature, whilst in others they can be heated for hours on the water-bath, and even maintained in the molten condition for a short time without undergoing transformation. The benzoyl derivatives are more stable than the corresponding acetyl compounds. In general, for some unexplained reason, the chemical nature of the substituent appears to have less influence on the stability of the derivative than has its position in the benzene nucleus. At present it is not possible to establish any definite connexion between the melting points and relative stabilities of the isomerides.

The stable acetyl and benzoyl derivatives are prepared by the action of warm acetic or benzoic anhydride on the indazoles. The labile compounds are obtained by the action of the requisite acid chloride on a suspension of the silver salt of the indazole in absolute ether; a few labile acetyl derivatives were prepared by the pyridine method. The following individual substances are described: 6-nitroindazole, m. p. 181° (2-acetyl derivative, stable form, m. p. 140—141°, labile *form*, colourless leaflets, m. p. 74—75°; 2-benzoyl derivative, stable form, m. p. 164—165°, labile *form*, yellowish-white, silky needles, m. p. 133—134° or 140° for different preparations). 6-Nitroindazole does not behave as definitely as indazole itself and its methyl derivatives towards methylating agents under varying conditions; thus, when heated with an excess of methyl iodide at 100°, it gives mainly 6-nitro-2-methylindazole, m. p. 159—160°, mixed, however, with 6-*nitro*-1-*methylindazole*, yellow, matted needles, m. p. 108—109°. When alkylation is effected in the presence of sodium methoxide, a mixture of the 1- and 2-methyl derivatives is likewise produced, the former being in excess. The constitution of 6-nitro-2-methylindazole is deduced by its reduction to 6-*amino*-2-*methylindazole*, long, intertwined needles, m. p. 156—157°, which, after diazotisation and elimination of the diazo-complex, yields 2-methylindazole. 5-Nitroindazole, m. p. 208°, gives a stable acetyl derivative, m. p. 158—159°, and a labile *compound*, long, slender, silky needles, m. p. 138—139°; the corresponding stable *benzoyl* derivative crystallises in pearly leaflets, m. p. 193—194°, whilst the labile *substance* forms prisms, m. p. 155°, when plunged into a bath pre-heated to 150°, but otherwise depending on the rate of heating. 4-Nitroindazole, m. p. 202—203°, is converted into stable and labile acetyl *derivatives*, colourless, silky needles, m. p. 144·5—145·5°, and small, pale yellow needles, m. p. 119—121°, respectively; the stable benzoyl compound has m. p. 162—163°, whilst the labile *form*, pale yellow, slender needles, has m. p. 130—132°. 4-Nitroindazole is reduced

by ferrous sulphate and excess of ammonia to 4-*aminoindazole*, colourless, shining leaflets, m. p. 150—151·5° (the *hydrochloride*, *nitrate*, *sulphate*, and *picrate*, greenish-yellow needles, which decompose without melting at 175—180° after darkening at 170°, are also described). 2-*Acetyl-4-acetylaminoindazole* is prepared in a stable modification, colourless, shining leaflets, m. p. 201—202·5°, and a labile form, pale yellow crystals, m. p. 155—160°. When either variety is warmed with dilute hydrochloric acid, 4-*acetylaminoindazole hydrochloride* is obtained in long needles, m. p. 223—225°, from which the free *base*, coarse prisms, m. p. 145—148°, is isolated in the usual manner. 4-*Cyanoindazole* forms yellow, flat needles, m. p. 157—160°. 7-Nitroindazole, m. p. 186·5—187·5°, yields a very readily hydrolysed, stable acetate, m. p. 132·5—134°; the corresponding labile variety could not be isolated with certainty, apparently owing to its extraordinary ease of hydrolysis.

5-Chloro-*o*-toluidine, b. p. 118—120°/18 mm., is converted into its *benzoyl* derivative, colourless needles, m. p. 165—166°, which is transformed through the *nitroso*-derivative into 5-*chloroindazole*, slender, shining needles, m. p. 119—120° (*picrate*, m. p. 193—195°); its stable and labile *acetates* have m. p.'s 144—145° and 119—120° respectively.

5-Methylindazole, m. p. 117°, is conveniently obtained from benzo-*m*-4-xylidide, which is converted into its unstable *nitroso*-compound, m. p. about 71—74°, which, when preserved in benzene solution, passes into the desired compound (picrate, thin, pale yellow needles or darker yellow needles grouped in rosettes, m. p. 169—170°). The stable *acetate* forms shining leaflets or flat needles, m. p. 49°, whilst the *labile* variety crystallises in colourless, transparent leaflets, m. p. 110—111°. The stable and labile *propionyl* compounds have m. p.'s 59—60° and 97—98° respectively, whilst the m. p.'s of the corresponding *benzoyl* derivatives are 89·5—90·5° and 120—121°. Treatment of 5-methylindazole with an excess of methyl iodide at 100° yields 2:5-*dimethylindazole*, coarse prisms, m. p. 76—77°, b. p. 270°/atmospheric pressure (the picrate, yellow, silky needles, m. p. 197—198°, mercuric chloride double salt, small, colourless prisms, m. p. about 220°, and silver nitrate additive *compound*, small, slender needles, m. p. 124·5—125·5°, are described). Alkylation with methyl iodide and sodium methoxide, on the other hand, appears to lead almost exclusively to the production of 1:5-*dimethylindazole*, colourless needles, m. p. 62—63° (*picrate*, m. p. 159—160°, mercuric chloride and silver nitrate additive *compounds*, m. p.'s 172—173° and 157—158° respectively). 6-*Methylindazole*, shining leaflets, m. p. 177—178° (*picrate*, m. p. 163·5—164·5°), forms an oily, stable *acetyl* compound, b. p. 146—147°/16 mm., and a labile *derivative*, colourless, shining leaflets, m. p. 116—118°. H. W.

A New Indigoid Dyestuff. 5-(Dioxy-2 : 4-pyrimidine)-2-indoleindigo [5(2′)-Indoxylpyrimidine-2 : 4 : 6-trione]. J. MARTINET and O. DORNIER (*Compt. rend.*, 1920, **171**, 184—187).

When some of the technical fusion of indoxyl is added to an acetic acid solution of alloxan heated on a water-bath, *5(2′)-indoxylpyrimidine-2:4:6-trione* is obtained in opaque, violet needles. It dyes wool and silk heliotrope, and even has a certain affinity for cotton. Its sulphonic derivative dyes wool and silk violet. To this compound the authors assign the constitution I, although this

$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{C{:}C}<\begin{matrix}\mathrm{CO-}\\ \mathrm{NH}\end{matrix}>\mathrm{C_6H_4} \qquad \mathrm{CO}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{N\cdot C}\leqslant\begin{matrix}\mathrm{CO}\\ \mathrm{N-}\end{matrix}>\mathrm{C_6H_4}$$

(I.) (II.)

constitution has already been assigned by Felix and Friedländer (compare A., 1910, i, 278) to a compound prepared by them from barbituric acid and isatin anilide. They contrast the properties of these two compounds, and consider that the constitution of the latter compound is better represented by formula II. W. G.

Fission of Organic Dyes by Hydrogenation. Richard Meyer (*Ber.*, 1920, **53**, [*B*], 1265—1276).—Alizarin direct violet R and alizarin direct green G of the Höchst Farbwerke are decomposed by hydriodic acid with the formation of leucoquinizarin and *p*-toluidine-2-sulphonic acid, and are thus isomeric with alizarin irisol and alizarin cyanine green G of the Farbenfabriken Friedr. Bayer & Co., which, when similarly treated, give leucoquinizarin and *p*-toluidine-3-sulphonic acid. It is remarkable that whilst *p*-toluidine-2-sulphonic acid condenses readily with quinizarin or leucoquinizarin, *p*-toluidine-3-sulphonic acid is unable to undergo such condensation, possibly because of internal salt formation between the neighbouring amino- and sulphonic groups.

The utility of concentrated hydriodic acid in effecting the fission of azo-dyes has been examined in a number of instances and its efficiency compared with that of sodium hyposulphite. In general, an aqueous or alcoholic solution of the dye is heated with an excess of concentrated hydriodic acid until action appears to be complete; the liberated iodine is removed by sulphurous acid and the hydriodic acid by evaporation with concentrated hydrochloric acid. The method has the great advantage over other reduction processes that it does not introduce any inorganic salts into the solution. Methyl-orange is decomposed by sodium hyposulphite or by hydriodic acid into *p*-aminodimethylaniline (acetyl derivative, m. p. 130°) and sulphanilic acid, whilst diphenylamine-orange gives *p*-aminodiphenylamine, m. p. 66°, and sulphanilic acid. Metanilic acid and *p*-aminodiphenylamine are obtained from metanil-yellow, whilst Congo-red yields benzidine and 1:2-naphthylenediamine-4-sulphonic acid. Naphthylene-red gives 1:5-naphthylenediamine and 1:2-naphthylenediamine-4-sulphonic acid. H. W.

New Catalytic Elements for the Transformation of Diazotised Compounds. A. Korczyński, W. Mrozinski, and W. Vielau (*Compt. rend.*, 1920, **171**, 182—184).—In certain of the changes brought about in the Sandmeyer reactions it is found

that the copper salt may quite well be replaced by the corresponding nickel or cobalt salt. Thus the double cyanide of nickel and potassium may replace that of copper and potassium for the preparation of nitriles from the corresponding diazonium salts. Cobalt is not satisfactory for this change.

Cobalt thiocyanate is an excellent catalyst for the conversion of diazonium salts into the corresponding thiocyanate, and in this case the intermediate double *compound* could be isolated from benzenediazonium chloride. It had the constitntion

$$(C_6H_5 \cdot N_2 \cdot CNS)_2, Co(CNS)_2,$$

and was obtained as a malachite-green, crystalline powder.

The preparation of chloro- or bromo-benzene from benzenediazonium chloride or bromide by the nickel or cobalt haloids only resulted in very poor yields, and took place only in boiling solution.

Zinc and iron salts showed no sign of any catalytic action for these changes. W. G.

Preparation of Methyl Red. LOUIS DESVERGNES (*Ann. Chim. anal.*, 1920, [ii], **2**, 209—210).—A solution of 89 grams of sodium nitrite in 150 c.c. of water is added slowly, with stirring, to a mixture of 137 grams of anthranilic acid, 1000 grams of water, 222 c.c. of hydrochloric acid (22°), and 300 grams of powdered ice. During the addition the temperature must not rise above 5°. After twenty minutes the mixture is added to 121 grams of dimethylaniline dissolved in 90 c.c. of hydrochloric acid (22°) and 200 c.c. of water, and, when the mixture has been stirred for a few minutes, 165 grams of sodium acetate dissolved in 500 c.c. of water are introduced. The purple-red crystals which form (in a few hours) are collected, washed with cold water, dried at 50°, and recrystallised from alcohol. W. P. S.

The Classification of the Proteins. PIERRE THOMAS (*Bull. Soc. chim. Biol.*, 1920, **2**, 112—118).—The existing classifications are reviewed, and the desirability of adhering to a simple and uniform international scheme is emphasised. J. C. D.

Barger's Microscopical Method of Determining Molecular Weights. II. Its Application to Caseinogen. KUMAO YAMAKAMI (*Biochem. J.*, 1920, **14**, 522—533).—The author confirms the observation of Robertson ("The Physical Chemistry of Proteins," 1918) that the molecular and ionic concentration of alkali caseinogenate solutions of neutral and alkaline reaction is conditioned by the concentration of the alkali solution in which the caseinogen is dissolved. The osmotic concentration of alkali caseinogenate solutions of acid reaction is dependent on the amount of dissolved caseinogen, and the mean weight of the ions in solution is about 2000.

The solubility of caseinogen in alkali solutions containing a certain amount of alkali chloride is almost twice that of caseinogen in pure alkali solution. This probably offers an explanation of the high solubility figures obtained by Robertson (*loc. cit.*) and Van Slyke

and Bosworth (A., 1913, i, 660). The true solubility of caseinogen in pure alkali must be $22 \cdot 5$—25×10^{-5} gram-equivalent alkali per gram caseinogen, and the molecular weight of alkali caseinogenate which is soluble in distilled water must be 4000—4400. W. G.

The Influence of Salts on the Optimum Condition of Precipitation of Caseinogen. L. MICHAELIS and ALBERT V. SZENT-GYÖRGYI (*Biochem. Zeitsch.*, 1920, **103**, 178—185).—The change in the optimum condition of precipitation of caseinogen by acetic acid and sodium acetate in the presence of salts is brought about by the action of the anion and the cation of the salts. When the action of the cation is stronger, the optimum flocculation is shifted to the less acid zone and vice versa. When the activity of both ions is the same no change in the optimum takes place. A table and curves of the results obtained with various salts are given. S. S. Z.

The Mode of Action of Chlorine on Oxyhæmoglobin. ANDRÉ MAYER and FRED VLÈS (*Bull. Soc. chim. Biol.*, 1920, **2**, 96—111).—A series of products are formed, which are characterised by their spectra, during the action of chlorine on hæmoglobin. It is probable that following the inhalation of large doses of chlorine the same series of reactions occurs as may be obtained in vitro. J. C. D.

Hæmocyanin. IV. Visible Absorption Spectrum of Oxyhæmocyanin. C. DHÉRE and A. BURDEL (*J. Physiol. Path. gen.*, 1920, **18**, 685—701).—The results of these spectrographic studies show that the oxyhæmocyanins of the gastropod molluscs of the cephalopods and of both the marine and fresh-water crustaceans give a clear and intense absorption band in the yellow when examined in suitable concentrations and solvents. The solutions examined were sufficiently clear and yet rich enough in pigment to give the characteristic band when intense illumination was employed. The solutions of oxyhæmocyanin do not contain tetronerythérin in appreciable quantities. Slight variations in the axis of absorption are considered as due to differences in the amounts of electrolytes present in the solutions examined. Photographs are appended. CHEMICAL ABSTRACTS.

Acidity of Ash-free and of Commercial Gelatin Solutions. H. E. PATTEN and T. O. KELLEMS (*J. Biol. Chem.*, 1920, **42**, 363—366).—The isoelectric point of ash-free gelatin lies at $p_H = 4 \cdot 8$, corresponding with a hydrogen-ion concentration of $1 \cdot 59 \times 10^{-5}$, and that of commercial gelatin at $p_H = 5 \cdot 64$, with hydrogen-ion concentration $2 \cdot 28 \times 10^{-5}$. The displacement of the isoelectric point of commercial gelatin is due to its alkali content. W. G.

Effect of Salts of Heavy Metals on a Protein and the Reversal of such Effects. ROBERT A. KEHOE (*J. Lab. Clin. Med.*, 1920, **5**, 443—452).—The coagulation of gelatin, under the

influence of salts of heavy metals, is not an irreversible reaction, but may be reversed through the action of alkalis or the neutral salts of the alkali and alkaline-earth metals. Not all such salts are of the same value in producing this effect, there being a marked secondary dependence on the acid radicle combined with the metal. Thiocyanates and iodides are more effective than bromides and chlorides. Reversal occurs most readily if the alkali or salt is added soon after the coagulation of gelatin by the heavy metal has been caused, and if heat is used. Coagulation of gelatin by heavy metals may be completely inhibited by the previous or simultaneous addition of alkalis or salts of the alkali or alkaline earth metals in sufficiently high concentrations, even when these are not of such nature as to combine with the coagulant. It is suggested that the metals react with the gelatin to form definite compounds as do the same metals with the fatty acids to form soaps. On the basis that the poisonous effects of the heavy metals on the body are due to coagulation of body proteins, the author believes that the administration of alkalis and salts of the alkali and alkaline-earth metals would be of benefit in lead and mercury poisoning, by reversing the coagulation of the proteins. CHEMICAL ABSTRACTS.

Relation between the Internal Complex Metallic Salts and the Solubility of Silk in Ammoniacal Nickel Solutions. The Biuret Reaction (Cu, Ni, Co) of Silk and Wool. M. BATTEGAY and THÉODORE VOLTZ (*Bull. Soc. chim.*, 1920, [iv], **27**, 536—540).—The colour changes and ultimate solution of silk when it is immersed in an ammoniacal solution of a nickel salt are explained as due to the formation of a complex nickel salt with a cyclic structure. The changes occurring are considered to be similar to those of the biuret reaction, and it is shown that under suitable conditions similar colour reactions may be obtained with silk and alkaline solutions of copper and cobalt salts.

When wool is dissolved in warm aqueous sodium hydroxide and to the solution an excess of copper sulphate is added, a rose-coloured liquid is obtained after filtration. Nickel salts give similar phenomena. Similar results are also obtained if the wool is first partly hydrolysed by acid and then treated with alkali and copper sulphate. W. G.

Does Chloropicrin Act on the Soluble Ferments? GABRIEL BERTRAND and (MME) ROSENBLATT (*Compt. rend.*, 1920, **171**, 137—139).—Chloropicrin was found to possess only a very slight inhibiting influence on the action of the various soluble ferments, sucrase, amygdalinase, urease, catalase, zymase, laccase, and tyrosinase, which were examined. W. G.

Silicon as a Substitute for Carbon in Organic Compounds. ARTUR BYGDÉN (*Diss.*, *Upsala*, 1916, pp. 189).—A historical summary of the chemistry of silicon compounds and their relation to the corresponding carbon compounds is given, followed by a study of the physical relations between the two classes of substances.

łono-derivatives, $RSiCl_3$, are easily obtained in most cases, disub-tituted derivatives are very difficult to prepare, whilst tetrasubsti-uted derivatives are the most easily obtained because an excess of he Grignard reagent can be used.

The b. p.'s under diminished pressure and the densities at different emperatures of the following compounds are recorded: $RSiCl_3$, vhere R = Et, Pr, butyl, *iso*butyl, *iso*amyl, Ph, and CH_2Ph; R_2SiCl_2, vhere R = Et and Pr; $RSiEtCl_2$, where R = Pr, *iso*butyl, and Ph; SiR_4, where R = Me and Et; SiR_3R', where R = Me or Et and R' = Et, Pr, butyl, *iso*butyl, *iso*amyl, Ph, and CH_2Ph; $SiMe_2R_2$, vhere R = Et and Pr; $SiMeEtR_2$, where R = Pr, *iso*butyl, and Ph; $CH_2{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}SiR_2$, where R = Cl and Me.

Benzyltrimethylmethanesulphonic acid, rectangular tablets with H_2O, m. p. (anhydrous) 142·2—144·2°, obtained by shaking the ydrocarbon with fuming sulphuric acid (6% SO_3), forms the ılts *ammonium*, *potassium* ($1H_2O$), *sodium* ($2H_2O$), *lithium* ($1H_2O$), *alcium* ($0·5H_2O$), *strontium* ($2H_2O$), *barium* ($3H_2O$), *magnesium* ($7H_2O$), *zinc* ($6H_2O$), *cadmium* ($3H_2O$), *ferrous* ($7H_2O$), *nickel* ($8H_2O$), *cobalt* (8[?]H_2O), *lead* ($2H_2O$), *copper* ($6H_2O$), and *silver* ($1H_2O$). The acid *chloride*, tablets or prisms, m. p. 58·7—59·2°, acid *romide*, m. p. 65·5—66°, *amide*, needles or scales, m. p. 101°, *nethylamide*, m. p. 94·8—95·3°, *anilide*, m. p. 137°, *methylanilide*, ı. p. 97·8—98°, *o-toluidide*, leaflets, m. p. 156—157°, *p-toluidide*, ı. p. 117—118·2°, and *benzylamide*, m. p. 141·5—141·7°, are escribed. By fusion with potassium hydroxide the potassium salt is onverted into *βββ-trimethylethylphenol*, $CMe_3\cdot CH_2\cdot C_6H_4\cdot OH$, eedles, m. p. 118—118·2°. CHEMICAL ABSTRACTS.

Physiological Chemistry.

Further Data Concerning the Alleged Relation of Catalase ɔ Animal Oxidations. RAYMOND L. STEHLE and ARTHUR C. ICCARTY (*J. Biol. Chem.*, 1920, **42**, 269—272. Compare A., 1919, 561).—Measurements were made of the carbon dioxide produc-on, and hæmoglobin and catalase contents of rabbit and cat blood rawn to correspond as nearly as possible with successive periods of ormal and high metabolism. Contrary to Burge's hypothesis (com-are A., 1919, i, 233), these experiments demonstrate that there ıay be great variations in the rate of animal metabolism without ny change in the catalase content of the blood. W. G.

Manganese Content of Human Blood and Tissues. LARENCE K. REIMAN and ANNIE S. MINOT (*J. Biol. Chem.*, 1920, **2**, 329—345).—See this vol., ii, 558.

Exchange of Chloride Ions and of Carbon Dioxide between Blood Corpuscles and Blood Plasma. L. S. Fridericia (*J. Biol. Chem.*, 1920, **42**, 245—257).—The author confirms the results of Van Slyke and Cullen (A., 1917, i, 521) as to the influence of the carbon-dioxide tension on the partition of the chlorides between plasma and red corpuscles, and shows that the cause of the exchange of chloride ions between plasma and corpuscles is in the red corpuscles and not in the plasma. The amount of chloride ions passing from the plasma into the corpuscles by increasing the carbon-dioxide tension from 0·08 to 162 mm. almost completely accounts for the increased carbon-dioxide combining power gained by the plasma. Increasing carbon-dioxide tension increases the carbon-dioxide combining power of both plasma and corpuscles, but the hydrogen-ion concentration remains almost the same in plasma and corpuscles at different carbon-dioxide tensions. Hasselbach's explanation of the properties of hæmoglobin (A., 1917, i, 490) offers an interpretation of both of these phenomena. W. G.

Metabolism of Carbohydrates. I. Stereochemical Changes undergone by Equilibrated Solutions of Reducing Sugars in the Alimentary Canal and in the Peritoneal Cavity. James Arthur Hewitt and John Pryde (*Biochem. J.*, 1920, **14**, 395—405).—See this vol., i, 508.

The Metabolism of Sulphur. III. The Relation between the Cystine Content of Proteins and their Efficiency in the Maintenance of Nitrogenous Equilibrium in Dogs. Howard B. Lewis (*J. Biol. Chem.*, 1920, **42**, 289—296).—A study of the relative efficiencies in nutrition of casein, a protein low in cystine content, and of serum albumin, high in cystine content, for dogs. Under conditions of low protein intake, serum albumin is more effective in maintaining nitrogenous equilibrium than is casein. When casein is supplemented by cystine, however, it is as efficient as serum albumin for the maintenance of nitrogenous equilibrium.
W. G.

The Fat-soluble Growth-promoting Substance in Lard and Cotton-seed Oil. Amy L. Daniels and Rosemary Loughlin (*J. Biol. Chem.*, 1920, **42**, 359—362).—Both lard and cotton-seed oil apparently contain appreciable amounts of the fat-soluble growth-promoting substance, as is shown by the growth of rats on a diet containing either of these fats and otherwise devoid of the fat-soluble vitamine. W. G.

Vitamine Studies. V. The Antiscorbutic Properties of Raw Beef. R. Adams Dutcher, Edith M. Pierson, and Alice Biester (*J. Biol. Chem.*, 1920, **42**, 301—310).—Guinea-pigs were fed on a diet of oats, water, and an amount of autoclaved milk sufficient to improve the diet, but insufficient to prevent scurvy. The animals developed scurvy and died. The addition of water extracts of raw, lean beef equivalent to 5, 10, 15, or 20 grams of

beef had no effect on the time of onset of scurvy or on the length of life of the animals. That the beef extract contained no deleterious ingredient was shown by the fact that when orange juice was added to the diet in addition to the beef juice, there was no scurvy and the animals were in excellent condition.

W. G.

Lipase of Pulmonary Tissue. André Mayer and Pierre Morel (*Bull. Soc. chim. Biol.*, 1919, **1**, 189—207).—Pulmonary tissue contains an enzyme which hydrolyses esters and glycerides, and has properties different from those of pancreatic lipase.

J. C. D.

Action of Extracts of the Spleen on the Smooth Muscle Tissues. Preparation and Nature of the Active Principle. L. Stern and E. Rothlin (*J. Physiol. Path. gen.*, 1920, **18**, 753—780).—The authors attempt to isolate the active principle of extracts of the spleen, which produces hypertonic conditions in organs containing smooth muscle tissue. Fresh spleens were cleaned from fat and connective tissue and ground to a pulp. The macerated tissue was boiled for half an hour in 2 to 3 vols. of water made slightly acid with acetic acid, and filtered. The filtrate was then heated just to the b. p., and sodium chloride and acetic acid were added until no more precipitation occurred. After filtering, the filtrate (usually clear) was evaporated on a water-bath to one-tenth the origiual volume. The material separating out on cooling was removed by filtration or centrifuging, and the liquid evaporated to dryness, powdered, and kept in a desiccator over sulphuric acid or calcium chloride. The product is soluble in water and very active in producing hypertonicity; 25 to 30 grams of substance result from 1 kilo. of spleen. The ethereal extract of the powder when dried and dissolved in salt solution is ineffective in producing contraction of smooth muscle. An extract of the powder made with slightly acidified ethyl alcohol is, however, quite as active as an equivalent amount of the original preparation. During the evaporation of the ethyl-alcoholic extract, insoluble material settles out, which is removed by filtration or centrifugation, and the residual liquor evaporated to dryness. A dark brown, hygroscopic powder results. The further purification of the compound is best effected by precipitation with phosphotungstic acid, and gives a product some sixty times as effective. The preparation is named "*liénine*" by the authors, who consider from physiological experiments that its action is through a direct effect on the smooth muscle fibres, thus differentiating it from adrenaline, which acts by intermediation of the nerve elements. Liénine is thus similar in action to β-amino-4-ethylglyoxaline. In view of these results, particular interest is attached to the spleen. It appears as if this organ can be considered as exercising an action on the general economy in retarding the exchanges and counterbalancing the action of other organs,

for example, the thyroid, such splenic function being due, in par least, to liénine, representing as it does a product of inte secretion or functional activity. CHEMICAL ABSTRACT

Evidence Indicating a Synthesis of Cholesterol by Infa JAMES L. GAMBLE and KENNETH D. BLACKFAN (*J. Biol. Che* 1920, **42**, 401—409).—For the estimation of cholesterol in n and stools, the authors recommend a modification of the met of Autenreith and Funk (*Münch. med. Woch.*, 1913, **60**, 12 the non-saponifiable material being separated from the soaps using diluted alcohol and light petroleum (compare Kumaga and Suto, A., 1908, ii, 331).

Analyses of the non-saponifiable fraction of infants' stools c firm the observation of Müller (compare A., 1900, ii, 289) that the case of infants on a continued milk diet, cholesterol is excre in the stools without undergoing change to any appreciable ext into coprosterol. From determinations of the cholesterol inta and excretion of four infants over a period of three days, duri which the subjects were gaining in weight and receiving a us amount of cholesterol, it is shown that the cholesterol excret was 1·7 to 3·4 times that which was present in the food.

W. G.

Decomposition of Propionic Acid in the Animal Bod LÉON BLUM and PIERRE WORINGER (*Bull. Soc. chim. Biol.*, 19 **2**, 88—95).—Lactic and pyruvic acids were found in the uri following the administration of propionic acid to dogs and rabbi These products probably arise in the body by oxidation of t α-carbon atom of the injected acid. The authors compare th with the oxidation of the α-carbon atom in the degradation of t α-amino-acid molecule in the animal organism. The questi whether lactic acid or pyruvic acid is the first to be formed is ful discussed, but an opinion is postponed until further researches ha been completed. J. C. D.

The Influence of Chemical Constitution on the Toxicit of Organic Compounds to Wireworms. F. TATTERSFIELD an A. W. R. ROBERTS (*J. Agric. Sci.*, 1920, **10**, 199—232).—Th authors have examined a very large number of organic compound with respect to their toxic action on wireworms, and from thei results certain general conclusions may be drawn as to the relation ship between chemical constitution and toxicity.

The general effect of a class of compounds of the same type i directly determined by the chemical constitution of the type, bu the particular effects of individual members of a class are limite by their physical properties, such as volatility. On the whole aromatic hydrocarbons and their halogen derivatives are more toxi than the aliphatic hydrocarbons and their halogen derivatives The substituents which influence toxicity most when introduce singly into the benzene ring are, in decreasing order of effective-

ness: methylamino-, dimethylamino-, hydroxy-, nitro-, amino-, iodine, bromine, chlorine, methyl groups. This order is, however, modified in the presence of a second substituent; thus, for example, when there is a methyl group already present in the ring, the order becomes: chlorine (in the side-chain), amino-, hydroxy-, chlorine (in the ring), methyl. When chlorine and hydroxy-groups are present together, they give rise to highly toxic substances, and the association of chlorine and nitro-groups in chloropicrin gives rise to one of the most toxic substances tested. Methyl groups introduced into the amino-group of aniline increase toxicity more than if substituted in the ring.

Compounds with irritating vapours, such as allylthiocarbimide, chloropicrin, benzyl chloride, usually have high toxic values, these values not being closely correlated with the vapour pressures or rates of evaporation of these substances.

There is a fairly close relationship between toxicity and vapour pressure, rate of evaporation, and volatility in the case of compounds of the same chemical type. Thus, in a series of similar compounds, decrease in vapour pressure and volatility is usually associated with an increase in toxicity. A limit is put on toxicity by the decrease in vapour pressure, which may sink too low to permit of a toxic concentration in the vapour phase. Chemically inert compounds boiling above 170° are usually uncertain in their toxic effect on wireworms, even after an exposure for 1000 minutes at 15°. Nearly all organic compounds boiling above 215° are uncertain in their action, whilst those boiling above 245° are non-toxic, although these limits depend to some extent on the resistance of the insect, the length of exposure, and the temperature at which the experiment is carried out. W. G.

Chemistry of Vegetable Physiology and Agriculture.

Action of a Bulgarian Ferment on Maltose and Sucrose. Gen Itsu Kita (*Bull. Soc. chim. Biol.*, 1920, **2**, 140—142).—This enzyme has no action on maltose or sucrose, as has previously been stated by Bertrand and Ducháček (A., 1909, i, 623).

J. C. D.

The Fermentation of Dextrose, Galactose, and Mannose by Lactobacillus pentoaceticus, n.sp. W. H. Peterson and E. B. Fred (*J. Biol. Chem.*, 1920, **42**, 273—287).—[With J. A. Anderson.]—The aldoses, dextrose, galactose, and mannose are fermented by *Lactobacillus pentoaceticus*, n.sp., with the production of lactic acid, ethyl alcohol, carbon dioxide, and small amounts of acetic acid. Dextrose and galactose are fermented at approxim-

ately the same rate and to the same extent, but mannose is more slowly attacked and less sugar is consumed. The difference is probably explicable by the configuration of the sugars.

The acetic acid obtained during the fermentation is probably produced by secondary fermentation of the lactic acid formed.

W. G.

The Nature of Yeast Fat. IDA SMEDLEY MACLEAN and ETHEL MARY THOMAS (*Biochem. J.*, 1920, **14**, 483—493).—Palmitic oleic, and linoleic acids have now been identified with certainty in yeast fat, but the pentadecoic acid previously described (Hinsberg and Roos, A., 1903, ii, 565; 1904, ii, 760) is a mixture of palmitic and lauric acids. An acid, m. p. 77°, was isolated (compare Neville, A., 1913, i, 1026), and is possibly arachidic acid. The authors were unable to confirm the presence of the dodecenoic acid described by Hinsberg and Roos (*loc. cit.*).

The sterol, present to the extent of about 20% of the total yeast, being partly in the free state and partly as fatty acid esters, is apparently identical with Tanret's ergosterol (A., 1889, 407). It is probable that the mycosterol isolated from certain fungi by Ikeguchi (this vol., i, 160) is also identical with ergosterol, and that this sterol is characteristic of the whole group of cryptogams. Yeast sterol is differentiated from the sterols of the higher plants and animals by the presence of three double bonds in its molecule.

W. G.

Water Culture Experiments with Different Nutrient Solutions; Influence of Manganese and Hydrogen-ion Concentration. FR. WEIS (*K. Vet.-Landbohöjskole Aarsskrift.*, 1919, 239—280; from *Chem. Zentr.*, 1920, iii, 99).—Manganese sulphate added to culture solutions in an amount equivalent to their normal iron content does not exert a beneficial influence on the growth of plants. The most favourable hydrogen-ion concentration for the classes of plants investigated was $p_H = 4 \cdot 5$—$6 \cdot 0$.

H. W.

Action of Chromium and Manganese on Plant Growth. TH. PFEIFFER, W. SIMMERMACHER, and A. RIPPEL (*Fuhling's Landw. Zeit.*, 1918, **17/18**, 313; from *Bied. Zentr.*, 1920, **49**, 259—263).—Experiments on oats and barley treated with an ordinary fertiliser and with small proportions of chrome iron ore or potassium dichromate fail to reveal any beneficial effect of the chromium (compare König, A., 1911, ii, 524). Similar experiments on oats treated with manganous sulphate indicate that the effect of the manganese is at most very minute.

T. H. P.

Are Vitamines Necessary for the Development of Plants? AUGUSTE LUMIÈRE (*Compt. rend.*, 1920, **171**, 271—273).—The author finds that fresh brewer's yeast heated to 135°, and no longer capable of curing polyneuritis in pigeons, gives a bouillon which considerably improves the development of fungi grown on poor culture solutions. As a result of these and further experiments, the

author concludes that vitamines, as ordinarily characterised, are not essential for the development of plants. W. G.

Chemical Components of Green Plants. II. Presence of a Mixture of Unsaturated Alcohols in many Green Plants. HARTWIG FRANZEN and ADOLF WAGNER (*Sitzungsber. Heidelberg Akad. Wiss. Math. nat. Klasse*, Abt. *A*, 1920, 2 reprints, pp. 4; from *Chem. Zentr.*, 1920, iii, 95).—The mixture of unsaturated alcohols found previously in the leaves of beech and chestnut is shown by its characteristic odour to be present also in the leaves of all classes of plants investigated (forty have been examined). The distillate from the mountain ash also contained hydrocyanic acid, whilst a component with an intense odour of lemons (citral) was present in that from strawberry leaves. The first distillate from certain plants (wormwood, dahlia, peppermint, ivy) contained notable amounts of essential oils. H. W.

The Presence of Copper in Plants and Particularly in Foodstuffs of Vegetable Origin. B. GUÉRITHAULT (*Compt. rend.*, 1920, **171**, 196—198).—The author has determined the percentage of copper present in a large number of fruits, vegetables, and seeds, and finds that the amount varies from 0·0087 to 0·0636% of the ash, and from 1·1 to 17·1 mg. per kilo. of fresh material. W. G.

The Odorous Constituents of Apples. Emanation of Acetaldehyde from the Ripe Fruit. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1920, **42**, 1509—1526).—The odorous constituents of apples were found to consist essentially of the amyl esters of formic, acetic, and hexoic acids, with a very small amount of the octoic ester. In addition, there was a considerable proportion of acetaldehyde and probably some free acid. The aqueous distillate from fresh apple parings also contained exceedingly small amounts of methyl and ethyl alcohols and furfuraldehyde, the latter probably arising from some chemical change during the distillation. The essential oil obtained from apple parings amounted to 0·0035% in the case of Ben Davis apples and 0·0043% in the case of crab apples.

Acetaldehyde is a product of the vital activities of the fruit, and occurs in the exhalations from ripe apples. W. G.

The Extraction of the Fat-soluble Factor of Cabbage and Carrot by Solvents. SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1920, **14**, 494—501).—Alcohol extracts the fat-soluble factor from cabbage and carrots. An amount of such extract equivalent to 10—12 grams of fresh carrots given daily is sufficient to promote normal growth in rats subsisting on a diet lacking the fat-soluble factor. In addition, the alcoholic extract from carrots contains the antineuritic and, to a smaller extent, the antiscorbutic factors. An ethereal extract from the alcoholic fraction equivalent to 25 grams of fresh carrots promoted recovery and renewed growth in rats

which were declining in weight on account of a fat-soluble factor deficiency. W. G.

The Occurrence of Water-soluble Vitamine in some Common Fruits. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1920, **42**, 465—489).—[With ALFRED J. WAKEMAN.]—The fresh juices of the edible parts of the orange, lemon, and grapefruit contain water-soluble *B* vitamine, the potency of the juices in this respect being similar, for equal volumes, to that of cow's milk. These juices may be suitably desiccated on starch without losing their efficiency. Grape juice was less potent than the fruit juices mentioned above. The edible portions of apples and pears furnish some water-soluble *B*, but from a comparative standpoint they cannot be regarded as rich in this factor; prunes are apparently somewhat richer.

From preliminary experiments it is doubtful whether the juices of lemon or grapefruit contain more than traces, if any, of the fat-soluble vitamine, though orange-juice would appear to contain some of this vitamine. W. G.

Spilanthol, the Pungent Principle of Para Cress (Spilanthes oleracea). I. YASUHIKO ASAHINA and MICHIZÔ ASANO (*J. Pharm. Soc. Japan*, 1920, No. 460, 503—515).—Gerber (A., 1903, ii, 609) isolated the pungent principle of Para cress, spilanthol, $C_{37}H_{64}O_3N_2$, as a syrup, which, when heated with alcoholic hydrochloric acid in a sealed tube, gave a base, $C_4H_{11}N$, and an acid, $C_{14}H_{28}O_2$. The authors prepared crude spilanthol (about 1%) from the air-dried flower-heads of the plant by Gerber's method. When kept it is changed into a resinous substance, and it becomes less soluble in ether. The base, $C_4H_{11}N$, formed by heating it with alcoholic hydrochloric acid, proved to be *iso*butylamine. Another decomposition product polymerised to a resinous substance. By shaking crude spilanthol in acetic acid solution in presence of platinum-black, it absorbs hydrogen gradually, with formation of *hydrospilanthol*; this is a colourless, viscous liquid with hay-like odour and bitter taste, which solidifies to crystals, m. p. 28°, is stable towards permanganate, and does not polymerise. It is probably a mixture of two substances, $C_{13}H_{27}ON$ and $C_{14}H_{29}ON$. By heating with alcoholic hydrogen chloride in a sealed tube, hydrospilanthol yields *iso*butylamine and a saturated fatty acid, m. p. 28° and b. p. 136—140°/4 mm.; probably a mixture of decoic acid, m. p. 31·5°, and nonoic acid, m. p. 12·5°. K. K.

The Toxicity of Iron and the Antitoxic Properties of Copper with Respect to Ferrous Salts. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, **171**, 218—222).—Ferrous salts are much more injurious to young plants than ferric salts. Any condition which tends to facilitate the oxidation of the ferrous to ferric salt consequently diminishes the toxicity of ferrous salts. This is the case with an addition of monopotassium phosphate, and particularly with an addition of copper sulphate, which has been

ɔown to exert a catalytic action on the oxidation of ferrous salts ɔompare this vol., ii, 547). W. G.

Comparative Study of the Microflora and Nitrogen ;ontent of Soils Partly Sterilised by Calcium Sulphide. ŀ. Truffaut and N. Bezssonoff (*Compt. rend.*, 1920, **171**, 68—271).—With a strong application of calcium sulphide and aphthalene or cymene to soil in porous pots, without a crop, this ërobic medium favours losses of ammoniacal nitrogen and is unıvourable to the development of anaërobic bacteria, such as *'acillus butyricus*. If the experiment is repeated with a crop resent, there is much less loss of nitrogen, whilst if the applica on is applied to soil in the field, crops being grown, it is found ıat there is a large increase in growth on the treated plot, no loss f nitrogen from the soil, and a considerable increase in the umbers of *B. butyricus* present. W. G.

Measure of the Ammonising Power of Arable Soil. ;. Perotti (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 251—256. ompare A., 1908, ii, 124).—The best conditions for carrying out ıe solution method of determining the ammonising power of rable soil are as follows: 10 c.c. of 1·5% peptone solution are ;eated in a test-tube with 5 c.c. of the solution, obtained by steepıg 50 grams of the soil in 500 c.c. of well-water. The tube is ept in a thermostat at 20—25° for four days, after which the mmonia produced is estimated by distilling the contents of the ıbe in presence of magnesium oxide. The mean of four separate eterminations is taken. T. H. P.

The Mechanism of the Decomposition of Cyanamide in he Soil. G. A. Cowie (*J. Agric. Sci.*, 1920, **10**, 163—176. 'ompare A., 1919, i, 376).—Cyanamide decomposes, in untreated ɔil or in soils previously heated to 120° or 135°, by a purely hemical change to carbamide. The subsequent conversion of the ırbamide to ammonia is brought about by soil organisms. In ;erile soils there is an accumulation of the carbamide, and this ıay also occur to a certain extent in soils under normal condiions. This decomposition of cyanamide appears to be more rapid ı clay soils than in sandy soils. In the case of an inert sand, in 'hich the cyanamide did not undergo decomposition, it was found ıat the addition of a zeolite, prehnite, resulted in the conversion f the cyanamide into carbamide.

Cyanamide does not appear to decompose in the manner ıdicated above in peat and fen soils; in these it gives rise to a ɜlatively small production of carbamide under normal conditions. W. G.

Solid Phases obtained by the Evaporation of certain Soil xtracts. M. S. Anderson and William H. Fry (*J. Ind. Eng. hem.*, 1920, **12**, 663—668).—The salts deposited on the evaporıion of the water extract of soils are of a much more complicated ıaracter than is indicated by a simple statement of the ions

existiug in solution. The deposited salts are similar to those obtained by natural or artificial evaporation of sea-water, but no soil can be expected to furnish all the salts occurring in natural deposits of saline substances, since these represeut crystallisation from a composite soil extract. As the salts begin to separate from the water extract at a point not far from the concentration corresponding with the moisture in an air-dry soil, it follows that the roots of growing plants may be in contact with solutions of these salts. Obversely, it is probable that the complex salts may be present in the soils only in solution in soil moisture, and never in the solid phase. W. P. S.

Substances Dissolved in Rain and Snow. Anon (*Chem. News*, 1920, **121**, 13—14. Compare Schutt and Dorrance, A., 1919, i, 116).—An account of analyses of rain and snow which fell in Mt. Vernon, Iowa, over the period October 9th, 1919, to May 22nd, 1920. During this period, 11·37 inches of rain fell and snow equivalent to 2·07 inches of rain, this in twenty-one precipitations of rain and eight of snow. Mt. Veruon is a town of 2,500 inhabitants, and is situated seventeen miles from the nearest industrial centre; it has no manufacturing industries. The analyses show that, during the period mentioned, 51·0306 lb. of sulphate as SO_3 fell per acre, the largest amount being 34 parts per million of water on March 4th, or 7·7137 lb. per acre. The total amount of chlorine was 48·1644 lb. per acre, equal to 79·36 lb. of sodium chloride. The largest concentration was in a slight snow storm, equivalent to 0·02 inch of rain, on December 2nd, when 17·7 parts per million were obtained, which is equivalent to 4·0157 lb. per acre. Nitrogen was determined in four forms: as nitrates (NO_3), nitrites (NO_2), free ammonia, and albuminoid ammonia. A total of 0·62841 lb. of nitrogen as nitrate fell, the greatest amount being 0·3 part per million, or 0·06806 lb. per acre, on December 2nd and January 23rd, at which times snow equivalent to 0·08 inch and 0·50 inch of rain fell, respectively. As nitrite, there was a total of 0·03725 lb. per acre, of nitrogen, the greatest amount being on March 19th, equal to 0·02 part per million of water, or 0·00453 lb. per acre; at this time 0·4 inch of rain fell. Free ammonia, equivalent to 2·8642 lb. of nitrogen, fell during the period; on March 4th, nitrogen as ammonia, equal to 2·30 parts per million, or 0·52181 lb. per acre, fell, with 0·4 inch of rain. Albuminoid ammonia was less frequent in its occurrence, for 32% of the rainfalls gave no reactions for this form. A total of 0·4974 lb. of nitrogen as ammonia in the albuminoid form fell, the greatest single amount coming on February 12th, when 1·12 parts of nitrogen per million, or 0·2541 lb. per acre, fell, with snow equal to 0·25 inch of rain. The total amount of nitrogen as free and albuminoid ammonia was 3·3616 lb. per acre. The total amount of nitrogen in all forms was 4·02726 lb. per acre, and of this, 82·5% was in the form of the two ammonias. J. F. S.

Organic Chemistry.

Weight of a Normal Litre of Propane. JEAN TIMMERMANS (*J. Chim. physique*, 1920, **18**, 133—141).—Propane was prepared by the action of sodamide on propyl iodide (Lebeau, A., 1905, i. 401, 501) or by the action of sodium on butyronitrile (Stahrfoss, *J. Chim. physique*, 1912, **10**, 497). The weight of a normal litre of the gas, prepared by either method, was found to be 2·0200 grams. W. G.

Preparation of Propylene and its Homologues. CHEMISCHE FABRIK BUCKAU (D.R.-P. 294794; from *Chem. Zentr.*, 1920, iv, 222).—A mixture of acetylene and its homologues with methane and its homologues is passed over a suitable non-metallic catalyst at 200—350°. The process may be carried out under increased pressure, or the mixture may be led through a contact apparatus completely filled with a porous catalyst. Titanic and silicic acids and their salts, as well as molybdic and tungstic acids, alumina, thoria, and zirconia, are recommended as catalysts. Examples are cited of the preparation of propylene from acetylene and methane, of butylene from acetylene and ethane, and of Δ^{β}-butylene from allylene and methane. H. W.

Conversion of Acetylene into Acetaldehyde and Acetic Acid. B. NEUMANN and H. SCHNEIDER (*Zeitsch. angew. Chem.*, 1920, **33**, 189—192).—For the conversion of acetylene into acetaldehyde on the laboratory scale, the best results were obtained by leading the gas, with vigorous mechanical stirring, into a catalyst composed of 96% acetic acid containing 3% of mercuric sulphate in solution, the temperature being maintained at about 30°. Under these conditions, nearly 90% of the theoretical yield was obtained. At 40—50°, the rate of absorption was actually greater, but the percentage yield of acetaldehyde was reduced to 70—80. Using a dilute sulphuric acid medium instead of acetic acid, the reaction was more erratic, and, in favourable circumstances, only 70—75% yields were obtained. The optimum temperature in this case was 25—30°, and a very great decrease in the rate of absorption and increase in the formation of polymerised and resinous by-products was observed when the temperature was raised at all above this point. The best results in the direct conversion of acetylene into acetic acid were obtained by using the above mercuric sulphate–acetic acid catalyst with the addition of vanadium pentoxide, acetylene and oxygen being led in alternately. Yields of acetic acid up to 83% were obtained. G. F. M.

Action of $\alpha\beta$-Chloroiodo-, Bromoiodo-, and Di-iodo-ethanes on the Sodium Sulphides. MARCEL DELÉPINE and LUCIEN VILLE (*Bull. Soc. chim.*, 1920, [iv], **27**, 678—679).—When sodium sulphide acts on $\alpha\beta$-chloroiodo-, bromoiodo-, or di-iodo-ethane in

aqueous or aqueous-alcoholic solution, ethylene, sulphur, and the sodium haloids are produced: $CH_2Cl\cdot CH_2I + Na_2S = NaCl + NaI + S + C_2H_4$. A similar reaction occurs if sodium hydrogen sulphide is used in place of the neutral sulphide. W. G.

Formation of Chlorohydrins. III. L. SMITH and E. SAMUELSSON (*Zeitsch. physikal. Chem.*, 1920, **94**, 691—722. Compare A., 1918, i, 370).—The present paper deals with the formation of monochlorohydrin, and is divided into two portions; the first deals with the formation from glycerol and hydrogen chloride, whilst the second treats of the action of hydrogen chloride on glycide. In the first case, twenty-three syntheses have been effected, with yields varying from 10—70% of the monochlorohydrin. It is shown that the lower the temperature the greater the yield of the α-chlorohydrin, and this is more noticeable if water is present from the beginning of the operation. Higher temperatures operate in the reverse way up to a certain point, which is probably to be explained by side reactions. In other words, the velocity with which hydrogen chloride attacks the secondary hydroxyl group has a greater temperature-coefficient than the velocity of the isomeric reaction. In the presence of succinic acid, and probably other catalysts, the α-isomeride is the chief product, whilst water, which retards the reaction, increases the yield of the β-isomeride. The catalyses by raising the temperature and by succinic acid are therefore opposed to one another. At those temperatures where the β-isomeride is formed in appreciable quantity, it is also decomposed rapidly, and much more so than its isomeride. It is possible by the following method to obtain a 40% yield of the pure α-isomeride: 0·5 gram-mol. of anhydrous glycerol containing 2 grams of succinic acid is treated with hydrogen chloride at 18° until there is an increase in weight of 18 grams. The addition of the hydrogen chloride takes place in two stages, with a pause of a day between the two additions. It is probable that a larger yield would be obtained if the mixture was kept longer. The unattacked glycerol may be regained in probably quantitative yield by distillation. The highest yield of the β-isomeride obtained was 15%. The best laboratory method for the preparation of glyceryl α-monochlorohydrin of approximate purity (1% β-isomeride) appears to be the following. Hydrogen chloride is passed into 1 gram-mol. of glycerol containing 4 grams of succinic acid until the weight has increased by 47 grams. The addition requires about eight hours, and the heat of the reaction keeps the temperature at 60—70°. The mixture should then be kept overnight. The yield in this case is 70%. If no special demands on the uniformity of the product are made, the reaction may be carried out at 120° until 39 grams of hydrogen chloride have been added. This gives a yield of 65%, and is much more conveniently carried out than the other methods.

The action of hydrogen chloride on glycide has been carried out in the following way: (i) leading hydrogen chloride into the pure glycide at −15°, 100°, and 140—145°; (ii) leading hydrogen

chloride in ethereal solutions of the glycide at −76°, −15°, and 25—27°; (iii) dropping the glycide into (*a*) ethereal solutions of hydrogen chloride, (*b*) acetone solutions of hydrogen chloride, and (*c*) concentrated hydrochloric acid, at −76°, −14°, 25—30°, 50—55°. The reaction velocity has been ascertained in each case. It is shown that at very low temperatures the chlorine enters the α-position by preference, but the reaction is never simply this, some of the β-isomeride always being produced. J. F. S.

Glyceryl β-Monochlorohydrin. L. SMITH (*Zeitsch. physikal. Chem.*, 1920, **94**, 723—738. Compare preceding abstract).—After discussion of a number of methods for the preparation of glyceryl β-chlorohydrin, the author recommends the following method of procedure. A mixture of 97 grams of 95% glycerol and 150 grams of concentrated hydrochloric acid is heated for five hours at 120°. This is then distilled at a pressure of 15 mm., and the fraction distilling at 110—150° collected. This fraction is pure chlorohydrin, and contains 14—15% of the β-isomeride. The product is purified by a long-continued fractional distillation under reduced pressure. The following physical properties are recorded: boiling point, α-isomeride, 119—119·5°/14·5 mm., β-isomeride, 124·5—125°/14·5 mm.; β-isomeride, D^0 1·3375, D^{20} 1·3207; α-isomeride, D^{20} 1·3213. The molecular weight by the cryoscopic method in water solution is 113 (theory, 110·5). J. F. S.

The History of Alcohol. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1920, **44**, 625. Compare A., 1913, i, 155, 244, 1298; 1918, i, 210).—The recent publication of Sudhoff confirms the author's previous conclusion that the distillation of alcohol was first effected in connexion with that of rose-water and not, apparently, by the followers of any official medical school. Distilled alcohol does not appear to have been made before the middle of the twelfth century. H. W.

Refractive Indices of Mixtures of *iso*Propyl Alcohol and Acetone. DOROTHY MURIEL PALMER (*Analyst*, 1920, **45**, 302).—Tables are given showing the refractive indices of mixtures of acetone and *iso*propyl alcohol containing from 0 to 100% of the latter. W. P. S.

Chloroformic Esters. G. CAPELLI (*Gazzetta*, 1920, **50**, ii, 8—12).—In order to obtain chloroformic esters in good yield by the action of carbonyl chloride on an alcohol, the former reagent must always be present in considerable excess. Good results may be obtained by using furnace coke, which is carefully dried, broken into pieces the size of peas, cooled by means of pounded ice, and saturated with carbonyl chloride. The flow of the gas is subsequently increased and the alcohol added in rapid drops. In order that the whole of the alcohol may be converted into ester and that the excess of carbonyl chloride may escape, the crude ester is left in a strong draught for about twenty hours, and is then

washed with ice-water, dried by means of calcium chloride, and fractionally distilled. The use of basic substances is unnecessary and the alcohol need not be anhydrous, 90% yields being obtained from alcohol of 76% concentration. T. H. P.

Improvements in Methods of Forming Esters. U.S. INDUSTRIAL ALCOHOL CO. (Brit. Pat. 147337).—Esters of the higher alcohols are produced by partial esterification in presence of a dehydrating agent, separating the latter, and continuing the esterification at a higher temperature. For instance, a mixture of 3205 grams of fusel oil (D 0·8268), 256 grams of concentrated sulphuric acid, and 2564 grams of glacial acetic acid is kept for twenty-four hours at the ordinary temperature with occasional agitation. The aqueous layer containing all the sulphuric acid is separated, and the oily layer distilled at 100° until no further separation of water occurs, indicating that esterification has ceased. The oily layer in the distillate is from time to time separated from the water and returned to the still, the contents of which are finally neutralised with 30% sodium hydroxide solution. The sodium acetate layer which separates is drawn off and distilled at 100° to recover any amyl acetate it may contain. G. F. M.

Anomalies in the Solidification Point of Tristearin. BEN H. NICOLET (*J. Ind. Eng. Chem.*, 1920, **12**, 741—743).—The double melting point of tristearin is attributed to the existence of two modifications, the more stable of which has m. p. 71·6—72·2°, and the unstable form about 55°, the latter being reconverted into the stable form on heating it at a higher temperature or allowing it to remain. In spite of the speed of solidification, the solidification point of tristearin is usually given as that of the unstable form (about 55°). The solidification point of pure tristearin was determined by the rise of temperature in Dalican's method. It first showed signs of solidification at 53·8°; the temperature then rose normally to about 63·5°, remained almost constant for some time, and then rose rapidly to the maximum at about 69°. On "seeding" liquid tristearin with the stable modification above 60°, solidification takes place without the formation of the unstable form, but the latter is apparently always produced after seeding, even with the stable form, at temperatures below 56°. Double solidification points are not necessarily shown by all the triglycerides which show a double melting point. It appears to be an essential condition that the solidification of the unstable form shall produce sufficient heat to reach the temperature of transition into the stable form. The phenomenon was shown by hydrogenated soya bean oil, but not by hydrogenated linseed or cotton-seed oil. The solidification point of hydrogenated linseed oil (65·9°) was not raised by "seeding." C. A. M.

Fat Associated with Starch. T. C. TAYLOR and J. M. NELSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1726—1738).—Corn starch, carefully freed from adherent or associated fat by repeated extraction

with ether, light petroleum, and carbon tetrachloride, gave on hydrolysis a material from which fat or free fatty acids could be extracted. The principal constituent of this "fat by hydrolysis" was palmitic acid, but there was, in addition, an unsaturated compound of unknown constitution. By controlled acid hydrolysis it was found that this fat was liberated when the hydrolysis had reached the erythrodextrin stage. Fat is also obtained by diastatic hydrolysis or hydrolysis with *Bacillus aceto-ethylicum*. By controlling the hydrolysis of the starch, it is possible to obtain residues containing relatively large amounts of fat combined with carbohydrate. Analytical data indicate that the palmitic acid is probably attached directly to the unsaturated componnd mentioned above in the form of an ester. Starches from other vegetable sources also contained varying amounts of "fat by hydrolysis," the amounts obtained varying from 0·04—0·83%. W. G.

Photochemical Chlorination of Methyl Sulphate. Preparation of Chloromethyl Sulphate. VOLMAR (*Bull. Soc. chim.*, 1920, [iv], **27**, 681—684).—Methyl sulphate readily undergoes chlorination at the ordinary temperature under the influence of ultra-violet rays, and more slowly under the influence of the light from an arc lamp or a metal filament lamp. The product is, in all cases, methyl chloromethyl sulphate, $CH_2Cl{\cdot}MeSO_4$. The fixation of a second chlorine atom is not possible, because it requires radiations of such a wave-length that the dichloromethyl sulphate is decomposed as it is formed. W. G.

Catalytic Oxidation by Unsaturated Compounds (Oils, Hydrocarbons, etc.). J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1920, **171**, 353—355).—When a solution of $\beta\beta'$-dichlorodiethyl sulphide in turpentine is exposed to air, the sulphide undergoes oxidation, giving $\beta\beta'$-dichlorodiethyl sulphoxide, $SO(C_2H_4Cl)_2$, m. p. 112°, which, when oxidised with potassium permanganate in acid solution, gives $\beta\beta'$-dichlorodiethylsulphone, $SO_2(C_2H_4Cl)_2$, m. p. 55°, and when treated with aqueous potassium hydroxide gives $\beta\beta'$-*dihydroxydiethyl sulphoxide*, $SO(C_2H_4{\cdot}OH)_2$, m. p. 111°. The turpentine may be replaced by various unsaturated oils and hydrocarbons. Similarly, when $\beta\beta'$-dihydroxydiethyl sulphide in solution in citraldehyde is exposed to air, it gives the dihydroxydiethyl sulphoxide described above.

That these oxidations are due to the catalytic action of the unsaturated solvents is shown by the fact that $\beta\beta'$-dichlorodiethyl sulphide in the pnre state or in solution in a saturated oil does not undergo oxidation when exposed to air. W. G.

Triethylene Tri- and Tetra-sulphides. (SIR) PRAFULLA CHANDRA RÂY (T., *1920*, **117**, *1090—1092*).

Optical Rotation of Dextrose under the Influence of Hydrochloric or Sulphuric Acid. I. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1920, **104**, 214—236).—Experiments with

hydrochloric acid at the ordinary temperature indicate that the influence of acid on the mutarotation of dextrose consists in an acceleration of the reaction to an extent increasing with the concentration of the acid; the accelerating effect of sulphuric acid is less than that of hydrochloric acid. The value of the final specific rotation increases with the proportion of acid present in the solution. Especially when the acidity is low, the rotation of dilute dextrose solutions is affected by hydrochloric acid less than that of more concentrated solutions. With the 10% acid, the specific rotation remains constant for a long time independently of the concentration; with the 20% acid, the rotation of dilute dextrose solutions does not change over a long period, but that of the more concentrated solutions gradually rises; 30% of hydrochloric acid produces a permanent increase in the rotation, this being greater for the high than for the low concentrations; 46% of the acid causes an initial increase in the rotation for the higher concentrations of the sugar, but continuous fall in the rotation soon begins, owing to decomposition of the dextrose. T. H. P.

Action of the Carbonates of the Alkaline Earths on Dextrose. II. Dextrose and Calcium Carbonate. Hans Murschhauser (*Biochem. Zeitsch.*, 1919, **99**, 190—204).—The modified dextrose obtained by boiling a solution of dextrose with calcium carbonate for three hours (this vol., i, 13) is fermentable. The presence of lævulose in it was demonstrated by Selivanov's reaction and by the separation of lævulose phenylmethylosazone by Neuberg's method. S. S. Z.

Dry Distillation in a Vacuum and its Application to the Study of Carbohydrates. Amé Pictet (*Bull. Soc. chim.*, 1920, [iv], **27**, 641—656).—A lecture delivered before the French Chemical Society.

The Ethylene-oxide Structure of Sucrose and some other Carbohydrates. Edward Frankland Armstrong and Thomas Percy Hilditch (T., 1920, **117**, 1086—1090).

Cellulose Acetate. H. J. H. Fenton and A. J. Berry (*Proc. Camb. Phil. Soc.*, 1920, **20**, 16—22).—The work described was mainly on the lines of investigating (*a*) substitutes for acetone as a solvent; (*b*) the influence of the mode of preparation on the properties of the product; (*c*) the characterisation and analysis of cellulose acetate.

No general conclusion can be drawn as regards the chemical nature of a liquid and its solvent action on cellulose acetate, although there appears to be some relation between the dielectric constant and solvent action. The authors consider that in Miles's method for the conversion of the cellulose acetate from an insoluble to an acetone-soluble form, partial hydrolysis, and not hydration, occurs. For the estimation of the acetyl group, the authors prefer Ost's method of cold alkaline hydrolysis (A., 1912, i, 680). W. G.

The Supposed Degradation of Starch by means of Formaldehyde. J. WOHLGEMUTH (*Biochem. Zeitsch.*, 1919, **99**, 316—320).—A final reply to Woker's criticism (this vol., i, 689).
S. S. Z.

Iron Salt of Carbohydrate-Phosphoric Acid. KARL SCHWEIZER (*Bull. Assoc. chim. Sucr.*, 1920, **37**, 464—468).—See this vol., i, 531.

Synthesis of Phytic Acid. R. J. ANDERSON (*J. Biol. Chem.*, 1920, **43**, 117—128).—The reaction between inositol, phosphoric acid, and phosphoric oxide has been again studied (compare Posternak, A., 1919, i, 433). The main product of this reaction appears to be an inositol ester of pyrophosphoric acid containing 4 atoms of phosphorus or 2 mols. of pyrophosphoric acid, and corresponding with the formula $C_6H_{12}O_{16}P_4$. This does not agree with the conclusion reached by Posternak (*loc. cit.*), who believed the chief product to be identical with the natural phytic acid or inositol-hexaphosphoric acid, $C_6H_{18}O_{24}P_6$.
J. C. D.

Complex Metallic Ammines. IV. *cis*-Sulphoacetato-, *cis*-Methionato-, and *cis*-Dimethylmalonato-diethylenediaminecobaltic Salts. THOMAS SLATER PRICE and JAMES COOPER DUFF (T., 1920, **117**, 1071—1077).

ψ-Muscarine ("Synthetic Muscarine"). ALBERT B. WEINHAGEN (*J. Amer. Chem. Soc.*, 1920, **42**, 1670—1678).—The action of nitric acid on choline platinichloride, according to the original directions of Schmiedeberg and Harnack (*Arch. expt. Path. Pharm.*, 1877, **6**, 101), gives as the principal product the platinichloride of choline nitrite (compare Ewins, A., 1914, i, 665), and *in addition a compound, m. p. 204—205°, which is probably* dimethylaminoethyl nitrate platinichloride and trimethylamine platinichloride. By deviating from the original directions by evaporating five times with nitric acid instead of only once, choline nitrite was not obtained, the main products being trimethylamine platinichloride and a compound, m. p. 208°, probably having the constitution $[NMe_3 \cdot CH_2 \cdot CH(OH)_2]_2PtCl_6$, assigned by Schmiedeberg and Harnack (*loc. cit.*) to "synthetic muscarine." In addition to the platinichloride, the derivatives of choline nitrite obtained were the *hydrochloride*, m. p. 165°, the *aurichloride*, the *sulphate*, the *perchlorate*, and the free *base*.

The pharmacological effects of "synthetic muscarine" reported by different observers must be considered with the above facts in mind.
W. G.

Manufacture of Complex Silver Salts of Aliphatic α-Amino-acids. HERMANN RICHARD NAPP (Brit. Pat. 148074).—Complex silver salts of aliphatic α-amino-acids are obtained by dissolving freshly precipitated silver oxide, or organic or inorganic salts of silver, in a solution containing an excess of the amino-acid

and allowing to crystallise, after suitable evaporation, if necessary, except in the case of the glycine compound, where crystallisation must be effected at temperatures below 0°, or otherwise the normal silver salt is obtained. These complex salts are more stable and more readily soluble in water than the normal salts, and do not give all the reactions of the silver cation, sodium hydroxide or carbonate, for instance, giving no immediate precipitation. The aqueous solutions are alkaline to litmus and do not precipitate albumin. The compounds have no irritating effect, and this, together with their other properties, renders them suitable for therapeutic purposes. G. F. M.

Decomposition of Glutamic Acid and its Salts on Heating. VLAD ŠKOLA (*Zeitsch. Zuckerind. Čechoslov.*, 1920, **44**, 347—351, 355—360, 363—368, 370—374).—Glutamic acid melts at 211° when very rapidly heated; when heated more slowly, or after prolonged drying at 110°, it shows a lower m. p., owing to slight decomposition (compare Menozzi and Appiani, A., 1894, i. 498). The conversion of *d*-glutamic acid into its lactam, *l*-glutimic acid (Staněk, A., 1912, i, 952), probably takes place to a slight extent when the former is simply dissolved in water. Equilibrium is attained in 2% solution after boiling for 100 hours, and 90—95% of glutimic acid is formed. The reaction is unimolecular. In presence of sulphuric or hydrochloric acid, the equilibrium is displaced in favour of glutamic acid; the displacement is a function of the concentration of mineral acid, and is much greater with hydrochloric than with sulphuric acid at the same concentration. Glutimic acid found in products of protein hydrolysis may thus be a secondary product only, and its amount may vary according as sulphuric or hydrochloric acid was used as hydrolyst. The pyrrolidone-2-carboxylic acid formula for glutimic acid is confirmed by the author's observation that this acid does not react with formaldehyde by Sörensen's method. The nitrogen of glutamic acid, on the other hand, reacts almost quantitatively provided that successive additions of formaldehyde are made alternating with neutralisation of the acidity developed by each addition. [See also *J. Soc. Chem. Ind.*, 1920, Oct.] J. H. L.

Synthesis of a Second Diamide, Oxamide, by Oxidation of Sucrose and Ammonia. R. FOSSE (*Compt. rend.*, 1920, **171**, 398—400).—When a solution of sucrose in strong ammonium hydroxide is oxidised by calcium permanganate, oxamide is obtained, and the course of the reaction is considered to be $2CH_2O \longrightarrow 2HCN \longrightarrow (CN)_2 \longrightarrow (CO{\cdot}NH_2)_2$. W. G.

The Constitution of Carbamides. XI. The Mechanism of the Synthesis of Urea from Ammonium Carbamate. The Preparation of certain Mixed Tri-substituted Carbamates and Dithiocarbamates. EMIL ALPHONSE WERNER (T., 1920, **117**, 1046—1053).

The Constitution of Carbamides. XII. The Decomposition of Urea when Heated in Solution in the Presence of Acids. EMIL ALPHONSE WERNER (*T.*, 1920, **117**, 1078—1081).

The Nature of the β-Ferricyanides and the β-Ferrocyanides. SAMUEL HENRY CLIFFORD BRIGGS (T., 1920, **117**, 1026—1034).

Estimation of Active Hydrogen in Organic Compounds. R. CIUSA (*Gazzetta*, 1920, **50**, ii, 53—55).—The method suggested by Moureu and Mignonac for diagnosing amines by treating them with magnesium ethyl bromide in ethereal solution and measuring the volume of ethane formed (A., 1914, i, 808) was first suggested by Tschugaev (A., 1903, i, 79) for the determination of the atoms of active hydrogen.

The author applies Moureu and Mignonac's experimental conditions to methyl alcohol, phenol, resorcinol, α-naphthol, pyrrole, 2-methylindole, phenylbenzylidenehydrazine, ethyl acetoacetate and ethyl ethylacetoacetate, nitromethane and nitroethane, the values obtained for the number of atoms of active hydrogen being either those required or in agreement with the results of previous investigators. 1-Methylpyrrole, 1-methylindole, and trinitrobenzene yielded no gas. T. H. P.

Reactions of certain Ortho- and Para-substituted Benzene Derivatives. A. ANGELI (*Gazzetta*, 1920, **50**, ii, 1—8; *Atti R. Accad. Lincei*, 1920, [v], **29**, i, 375—381).—The author has shown previously (A., 1917, i, 452) that hydrogen peroxide, hydroxylamine, and hydrazine exhibit chemical analogy to quinol, *p*-aminophenol, and *p*-phenylenediamine, and that in some reactions of ortho- and para-substituted aromatic compounds, the two substituent groups behave as though directly joined. Further examples of such analogy are now given.

The reaction between a ketone and ethyl oxalate, $R{\cdot}COMe + (CO_2Et)_2 \longrightarrow R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$, is quite analogous to that between *o*- or *p*-nitrotoluene and the ester, $C_6H_4Me{\cdot}NO_2 + (CO_2Et)_2 \longrightarrow NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$. With the aliphatic compounds, it is the negative group (CO, CN, etc.) which impresses increased mobility on the hydrogen atoms of the methyl group, whereas with the aromatic compounds this purpose is served by the nitro-group, which enhances the negative character of the whole of the aromatic residue.

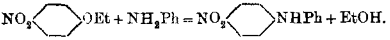
The hydrolysis of certain methylamine derivatives, with formation of diazomethane, $NHMe{\cdot}COR \longrightarrow NO{\cdot}NMe{\cdot}COR \longrightarrow CH_2{:}N{:}N$, is similar to the behaviour of analogous derivatives of *o*-toluidine, which yield indazole,

$$C_6H_4Me{\cdot}NH{\cdot}COR \longrightarrow C_6H_4Me{\cdot}N(NO){\cdot}COR \longrightarrow C_6H_4{<}{}^{CH_2}_{N}{>}N.$$

The transformations produced in certain *o*- and *p*-substituted nitro-derivatives, for instance,

$$NO_2{\cdot}C_6H_4{\cdot}NO_2 + H_2O = NO_2{\cdot}C_6H_4{\cdot}OH + HNO_2$$

and $NO_2{\cdot}C_6H_4Cl + H_2O = NO_2{\cdot}C_6H_4{\cdot}OH + HCl$, correspond with those exhibited by N_2O_4 and NO_2Cl. Further, the formation of phenylnitroamine from ethyl nitrate and aniline, $NO_2{\cdot}OEt + NH_2Ph = NO_2{\cdot}NHPh + EtOH$, *is analogous to the reaction*



Another group of transformations indicating the connexion between two ortho- or para-substituents is that in which one or both of the oxygen atoms of a nitro-group migrate to a carbon atom. Among these are (1) the formation of *p*-aminobenzaldehyde by the action of alkali sulphide on *p*-nitrotoluene, (2) the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid under the influence of light, (3) the transformation of *o*-nitrotoluene into *o*-nitrosobenzyl alcohol, and (4) that of *o*-nitrotoluene into anthranilic acid by the action of an alkali. Owing to the marked alterability of the aromatic hydroxylamines and the different behaviour of aliphatic aldehydes and nitro-derivatives, it is not always possible to realise the analogous transformations in the two series, but nitromethane, for instance, readily undergoes the following changes: $NO_2Me \longrightarrow OH{\cdot}NH{\cdot}CHO \longrightarrow NH_2{\cdot}CO_2H \longrightarrow NH_3 + CO_2$.

A parallel to the oxidation of aliphatic nitro-derivatives, $2NO_2{\cdot}CH_2R \longrightarrow NO_2{\cdot}CHR{\cdot}CHR{\cdot}NO_2$, is found with *o*- and *p*-nitrotoluenes, which undergo a similar change without oxidising agents, the oxidation being effected by part of the nitro-compound itself, $2NO_2{\cdot}C_6H_4Me \longrightarrow NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$. In the case of nitromethane, another product, metazonic acid, containing one oxygen atom less, is also obtained.

Analogies also appear between the physiological behaviour of certain corresponding derivatives of the aliphatic and aromatic series. Thus, ethylurethane exerts a hypnotic action, whereas ethyl *p*-aminobenzoate acts as an anæsthetic. Further, hydrazine is poisonous, as also is *p*-phenylenediamine. Aliphatic diamines, such as putrescine and cadaverine, are, however, physiologically inert, and the conclusion is drawn that the same holds for 1 : 4-diamino*cyclo*hexane. T. H. P.

Preparation of Picryl Chloride by Nitration of 4-Chloro-1 : 3-dinitrobenzene. PERCY FARADAY FRANKLAND and FREDERIC HORACE GARNER (*J. Soc. Chem. Ind.*, 1920, **39**, 257—260T).—For the preparation of picryl chloride from chlorodinitrobenzene, it is recommended to use 100 grams of chlorodinitrobenzene, 750 grams of 100% sulphuric acid, and 125 grams of 90% nitric acid, the nitration being conducted at 130° for twelve hours. If 96% sulphuric acid is used, the amount must be doubled and the amount of nitric acid increased to 175 grams. A portion of the chlorodinitrobenzene is oxidised, the ratio of the amount of nitric acid used in nitration to the amount used in oxidation being 1 : 1·8.

W. G.

Organic Molecular Compounds. IV. Addition of Alkyloxy- to the Nitro-group. M. Giua and A. Marcellino (*Gazzetta*, 1920, **50**, i, 341—359. Compare A., 1916, i, 205).—In order to ascertain if the property of forming more or less intensely coloured additive compounds with polynitro-derivatives exhibited by aromatic compounds containing a phenolic hydroxyl group persists when the hydroxyl is etherified, the authors have investigated cryoscopically the binary systems formed by *m*-dinitrobenzene, 2 : 4-dinitrotoluene, 2 : 4 : 6-trinitrotoluene, and picric acid with β-naphthol methyl ether and the dimethyl ether of quinol.

The results obtained show that 2 : 4 : 6-trinitrotoluene and picric acid, but not *m*-dinitrobenzene or 2 : 4-dinitrotoluene, form compounds with the ethers mentioned. With the exception of that formed from the dimethyl ether of quinol and picric acid, the nature of the additive compound does not depend on the number of alkyloxy-groups present. Further, the presence of the double ring in β-naphthol is without influence on the formation or non-formation of the additive compound, this observation being in agreement with Sudborough's conclusion that, as regards the property of forming additive compounds, a condensed system of two or more benzene rings may be considered as a single ring (T., 1916, **109**, 1339).

The molecular compounds which 2 : 4 : 6-trinitrotoluene and picric acid form with β-naphthol methyl ether and the dimethyl ether of quinol show intense coloration varying from pale yellow to orange-yellow. As in certain similar cases, the colour of the compound is related to the auxochrome group, but for the formation of the compound and of the colour the presence of three nitro-groups in one of the two components is a necessary condition. Which of the three nitro-groups is added to the alkyloxy-group has not yet been established, but from Werner's conception that mutual saturation of the secondary valencies of the chromophore and auxochrome groups must be assumed in the molecular compounds (A., 1910, i, 20), it seems probable that the additive compounds now described are formed by means of the valencies between the characteristic functional groupings; the influence of the aromatic nucleus must not, however, be overlooked. These results are discussed in relation to those obtained by Giua and Cherchi (this vol., i, 303).

The system *m*-dinitrobenzene : β-naphthol methyl ether forms a single eutectic, m. p. about 42°, containing 50% by weight of the nitro-compound. 2 : 4-Dinitrotoluene : β-naphthol methyl ether, one eutectic, m. p. about 34°, 57% of nitro-compound. 2 : 4 : 6-*Trinitrotoluene : β-naphthol methyl ether forms a compound*, m. p. about 73°, containing 1 mol. of each component; the eutectic between the compound and the trinitrotoluene has m. p. about 60°, and that between the compound and the ether m. p. 58°. Picric acid (1 mol.) and β-naphthol methyl ether (1 mol.) form a compound, m. p. about 114°, the eutectics between this compound and the picric acid and ether melting at 99° and 67·4°

respectively. *m*-Dinitrobenzene : dimethyl ether of quinol gives a single eutectic, m. p. about 30°, at a concentration of 50%. 2:4-Dinitrotoluene : dimethyl ether of quinol forms one eutectic, m. p. about 30°, at a concentration of 50%. 2:4:6-Trinitrotoluene (1 mol.) and the dimethyl ether of quinol (1 mol.) form a compound, m. p. 43·3°, the eutectics between this compound and the nitro-compound and ether melting at 42·2° and about 38° respectively. Picric acid (2 mols.) and the *dimethyl ether* of quinol (3 mols.) form a compound which has an indistinct melting point and dissociates on melting. *m*-Dinitrobenzene (1 mol.) and *β*-naphthol (1 mol.) give a compound, m. p. about 62° (dissociating). 2:4-Dinitrotoluene (1 mol.) and *β*-naphthol (1 mol.) form a compound, m. p. 76·6°, the eutectics between this compound and the compouents melting at about 59° and about 74° respectively. 2:4:6-Trinitrotoluene (1 mol.) and *β*-naphthol (1 mol.) give a compound, m. p. 109·4°, the eutectics between this compound and the components melting at 73·5° and 97·5° respectively.

The fused mixtures of the nitro-compounds examined with the ethers of *β*-naphthol and quinol and with *β*-naphthol are all more or less intense yellowish-red. Only for the systems in which a single eutectic appears are the mixtures pale yellow in the hot and almost colourless when cold. T. H. P.

4-Nitro-*o*-toluenesulphonic Acid. S. V. Hintikka (Can. Pat. 200291).—This acid is prepared by sulphonating *p*-cymene to its *o*-sulphonic acid and treating the sulphonation mixture at 40—60° with nitric and sulphuric acids; the *iso*propyl group is thus replaced by the nitro-group. Chemical Abstracts.

Condensation of Salicylaldehyde and Thymol. Synthesis of *o*-Hydroxyphenyldithymylmethane. F. Lavilla Llorens (*Anal. Fis. Quim.*, 1920, **18**, 139—147).—The object of the investigation is to prepare triarylmethanes with a hydroxyl group on each benzene nucleus, and to study their physicochemical properties. The first of these compounds to be prepared is *o-hydroxyphenyldithymylmethane*, $OH·C_6H_4·CH(C_6H_2MePr^{\beta}·OH)_2$, colourless, oblique prisms containing 1EtOH, m. p. 185°, from salicylaldehyde and thymol in presence of a small quantity of sulphuric acid. The *triacetyl* and *tribenzoyl* derivatives and the *trimethyl* and *triethyl* ethers are described; the last three compounds have m. p. 126—127°, 137—138°, and 77—78° respectively. A *tribromo*-derivative, $C_{27}H_{29}O_3Br_3$, m. p. 170°, is obtained in acetic acid solution. The corresponding *tri-iodo*-compound has m. p. 111°. The *trisodium* salt, $C_{27}H_{29}O_3Na_3$, crystals, is decomposed slightly by carbon dioxide. Amorphous precipitates are obtained: with lead salts, light yellow; copper salts, bluish-green; and ferric salts, yellowish-brown. W. R. S.

Molecular Compounds of Sulphur Dioxide with Amines. A. Korezynski and M. Glebocka (*Gazzetta*, 1920, **50**, i, 378—387).—The following compounds of sulphur dioxide with

amines have been prepared: with *p*-toluidine, $C_7H_7 \cdot NH_2,SO_2$, canary-yellow; α-naphthylamine, $C_{10}H_7 \cdot NH_2,SO_2$, orange-yellow; *p*-chloroaniline, $C_6H_4Cl \cdot NH_2,SO_2$, canary-yellow; *p*-bromoaniline, $C_6H_4Br \cdot NH_2,0 \cdot 5SO_2$ and $C_6H_4Br \cdot NH_2,SO_2$, canary-yellow; 3:5-dichloroaniline, $C_6H_3Cl_2 \cdot NH_2,SO_2$; 2:4-dichloroaniline,

$C_6H_3Cl_2 \cdot NH_2,SO_2$,

canary-yellow; 3:5-dibromoaniline, $C_6H_3Br_2 \cdot NH_2,SO_2$, canary-yellow; *p*-nitrosodiethylaniline, $C_8H_{10}O_2N_2,2SO_2$; diphenylamine, $C_{12}H_{11}N,0 \cdot 5SO_2$, orange; α-naphthaquinoline, liquid compound; γ-chloroquinaldine, $C_{10}H_8NCl,1 \cdot 5SO_2$; aminoazobenzene,

$C_{12}H_{11}N_3,SO_2$;

dimethylaminoazobenzene, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot NMe_2,0 \cdot 5SO_2$; dimethylaminoazobenzoic acid, $CO_2H \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NMe_2,SO_2$; thiocarbamide, $CH_4N_2S,0 \cdot 5SO_2$, colourless; ethyl *p*-aminobenzoate,

$C_8H_{11}O_2N,0 \cdot 5SO_2$,

canary-yellow; *o*-aminocinnamic acid, $C_9H_9O_2N,SO_2$, pale yellow; 2:4-tolylenediamine, $C_7H_{10}N_2,SO_2$, canary-yellow; *p*-nitro-*m*-phenylenediamine, $C_6H_7O_2N_3,0 \cdot 5SO_2$, yellow; benzidine,

$C_{12}H_{12}N_2,2SO_2$,

canary-yellow; 1:3-diaminoazobenzene, $C_{12}H_{12}N_4,0 \cdot 5SO_2$; tetramethyldiaminotriphenylmethane, $C_{25}H_{26}N_2,2 \cdot 5SO_2$; leucaniline, $C_{20}H_{21}N_3,3SO_2$, pale yellow; *p*-leucaniline, $C_{19}H_{19}N_3,1 \cdot 5SO_2$, pale yellow; rosaniline, $C_{20}H_{21}ON_3,1 \cdot 5SO_2$; pararosaniline,

$C_{19}H_{19}ON_3,SO_2$;

dimethylaminoacetanilide, $C_{13}H_{17}ON_3,SO_2$, canary-yellow; hexamethylenetetramine absorbs 36·6—37·8% SO_2, giving a colourless product of no definite molecular composition; caffeine,

$C_8H_{10}O_2N_4,0 \cdot 5SO_2$,

colourless; strychnine, $C_{21}H_{22}O_2N_2,2SO_2$, pale yellow; brucine, $C_{23}H_{26}O_4N_2,3SO_2$, yellow; morphine, $C_{17}H_{19}O_3N,1 \cdot 5SO_2$, canary-yellow; quinine, $C_{20}H_{24}O_2N_2,SO_2$, lemon-yellow; papaverine, $C_{20}H_{21}O_4N,SO_2$, straw-yellow; veratrine, $C_{32}H_{49}O_9N,2 \cdot 5SO_2$, yellow; hæmatin, $C_{32}H_{32}O_4N_4Fe,2 \cdot 5SO_2$; atropine, cocaine, and narcotine form liquid additive compounds with sulphur dioxide, and no additive compounds are given by *o*-, *m*-, and *p*-nitroanilines, 2:4- and 3:5-dinitroanilines, trinitroaniline, 6-halogeno-2:4-dinitroanilines, *p*-nitrosoaniline, trihalogenated anilines, *m*- and *p*-nitrodimethylanilines, azobenzene, benzeneazonaphthyl ethyl ether, dimethylaminoazonitrobenzoic acid, carbamide, acetamide, benzamide, asparagine, thiocarbazide, acetanilide, acetophenetidide, α-aminopropionic acid, α-amino*iso*hexoic acid, aminobenzoic acids, sulphanilic acid and its sodium salt, propyl *p*-aminobenzoate, *m*- and *p*-aminocinnamic acid, *o*-, *m*-, and *p*-aminophenols, *p*-chloro-*o*-aminophenol, ethyl *p*-amino-*m*-hydroxybenzoate, methyl *m*-amino-*p*-hydroxybenzoate, carbazole, *p*-benzoquinone, distyryl ketone, theobromine, and hæmin.

When kept in a desiccator, the above additive compounds lose sulphur dioxide; measurements of the pressures developed in this way are now being made.

The following general conclusions are drawn from the results obtained. Sulphur dioxide unites equally with primary, secondary,

and tertiary amines. Colourless amines containing an aromatic nucleus yield yellow additive compounds, whilst those free from such nucleus give colourless compounds. The appearance of the colour indicates the formation of secondary compounds, which are produced by virtue of the secondary valencies of the nitrogen atom. The action of such secondary valencies is diminished or entirely removed by the presence of negative substituents in the molecule, the influence of a nitro- or hydroxyl group being greater than that of a halogen atom. No direct dependence exists between the number of amino-groups and the number of molecules united with SO_2. In compounds of complicated structure, such as the alkaloids, the number of molecules united with SO_2 is mostly greater than the number of nitrogen atoms.

When thoroughly dried reagents are used, carbon dioxide and hydrogen sulphide do not form additive compounds with *p*-toluidine, *a*-naphthylamine, *a*-naphthaquinoline, brucine, hæmin, or hæmatin. Similar failure to form compounds, even with ferrous sulphate and ferrous ammonium sulphate, is exhibited by nitric oxide.

T. H. P.

Syntheses of *s*-Xylidine. HERBERT L. HALLER, ELLIOT Q. ADAMS, and EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1920, **42**, 1840—1842).—*s*-Xylidine may be prepared from mesitylene by passage through mesitylenic acid and its amide, the latter being converted into the amine by Hofmann's reaction. A more satisfactory process is a modification of that of Willgerodt and Schmierer (A., 1905, i, 425), starting from *m*-4-xylidine. The authors find that, in this process, nitroacetylxylidide may be converted directly into nitroxylene by heating the xylidide for fifteen minutes with sulphuric acid (D 1·84), pouring the product into a mixture of ethyl alcohol and sulphuric acid, diazotising with sodium nitrite, and distilling the product with steam in the presence of copper powder. *s*-Xylidine has m. p. 139·6—140·2°, n_{α} 1·45, n_{γ} 1·69

W. G.

Separation of *a*-Aminophenyl-*a*-naphthylmethane into its Optical Antipodes. S. BERLINGOZZI (*Gazzetta*, 1920, **50**, ii, 56—59).—This compound, obtained as the racemic modification (this vol., i, 480), may be separated into its enantiomorphous components by fractional crystallisation of the tartrates from alcoholic solution.

d-*a-Aminophenyl-a-naphthylmethane hydrogen tartrate*,

$$C_{17}H_{15}N,C_4H_6O_6,$$

forms shining, white scales, m. p. 190—207° (decomp.). The free d-*base*, $C_{17}H_{15}N$, crystallises in white, translucent, triangular, or trapezoidal prisms, m. p. 81—82°, $[\alpha]_D^{15}$ +63·61°. The *hydrochloride*, $C_{17}H_{15}N,HCl$, forms silky, white needles, m. p. 275—280° (decomp.), $[\alpha]_D^{5}$ −53·43°.

l-*a-Aminophenyl-a-naphthylmethane hydrogen tartrate* forms tufts of white needles, m. p. 195—210° (decomp.). The free l-*base* crystallises in white, translucent, triangular prisms, m. p. 81—82°, $[\alpha]_D$ −63·38°. The *hydrochloride* forms silky, white needles, m. p. 275—280°, $[\alpha]_D$ +53·18°.

T. H. P.

Amines. VIII. The Preparation of ω-Aminoacetanilide. ARTHUR J. HILL and ERWIN B. KELSEY (*J. Amer. Chem. Soc.*, 1920, **42**, 1704—1711. Compare Dubsky and Granacher, A., 1918, i, 189).—To obtain a satisfactory yield of ω-aminoacetanilide, the authors found it necessary to modify Majert's process (D.R.-P. 59121). The chloroacetanilide (550 grams) was added to 11 kilos. of 95% alcohol previously saturated with ammonia. The mixture was kept for five days at 20°, and then evaporated under diminished pressure to one-quarter of its volume. The liquid was poured into 3·5 litres of water, and the oil which separated was filtered after it had solidified. Aminoacetanilide was obtained from the filtrate by evaporating it nearly to dryness, and then recrystallising the residual material from water. The oil which separated and then solidified, as described above, was iminodiacetanilide,

$$(NHPh\cdot CO\cdot CH_2)_2NH.$$

In some preparations, a small amount of *nitrilotriacetanilide*, $(NHPh\cdot CO\cdot CH_2)_3N$, m. p. 238—239°, was isolated.

The authors were unable to obtain satisfactory yields of aminoacetanilide by Majert's process (D.R.-P. 59874) from aniline and ethyl aminoacetate hydrochloride. W. G.

Preparation of "Cupferron." D. R. KASANOF (*J. Ind. Eng. Chem.*, 1920, **12**, 799).—The yield of the intermediate substance, phenylhydroxylamine, in the preparation of "cupferron" (A., 1911, ii, 939) depends on the quality of the zinc dust used to reduce the nitrobenzene, but consistently good yields may be obtained if the zinc dust is previously treated with 2% mercurous nitrate solution slightly acidified with nitric acid. W. P. S.

Crystallographic Properties of some Catechol Derivatives of Acids of Heavy Metals and their Salts. P. J. BEGER (*Centr. Min.*, 1920, 129—142).—The compounds, the crystallographic properties of which are described in considerable detail, were prepared by Weinland and his collaborators (A., 1919, i, 442).

Tricatechol arsenate [catechol semiarsenate],

$$AsO(O\cdot C_6H_4\cdot OH)_3,4H_2O,$$

small, shining, colourless crystals of cubic habit, belonging to the rhombic, bipyramidal system, $a:b:c=0·958:1:0·988$. There are perfect cleavages parallel to the three pinacoid faces. Optic axial plane, {010}. The chromium salt, $[AsO(O\cdot C_6H_4\cdot O)_3]_3H_6Cr,12H_2O$, the cobalt salt, $[AsO(O\cdot C_6H_4\cdot O)_3]_2H_4Co,8H_2O$, and the corresponding nickel salt, all crystallise in the cubic system. The sodium salt of the nickel derivative, $Ni(O\cdot C_6H_4\cdot ONa)_2,12H_2O$, forms greenish-black, monoclinic, prismatic crystals, the axial ratios of which could not be completely determined; $a:b:c=1·19:1:?$; $\beta=102·5°$ approx. Ammonium catechol molybdate,

$$OH\cdot MoO_2\cdot O\cdot C_6H_4\cdot ONH_4,\tfrac{1}{2}H_2O,$$

forms reddish-black prisms, rhombic bipyramidal, $a:b:c=0·5890:1:0·9105$. The crystals, which sometimes show vicinal faces with complex indices, cleave perfectly parallel to {010} and {001}.

E. H. R.

Quinol. J. Messner (*Pharm. Zentr.-h.*, 1920, **61**, 454—455).—The statement found generally in literature that quinol reduc Fehling's solution in the cold and silver nitrate only when heat is incorrect. Quinol reduces silver nitrate at the ordinary tempera ture, with the separation of metallic silver; it at once changes th colour of Fehling's solution to green, but a precipitate of cuprou oxide forms only after long contact or when the mixture is heate The reactions are therefore of little use for distinguishing quin from catechol. W. P. S.

Amino-alcohols Derived from α-Anilino-γ-dialkylaminoisopropyl Alcohols. E. Fourneau and J. Ranedo (*Anal. Fis. Quim* 1920, **18**, 133—139).—The physiological effect of the replaceme of a phenoxy- by an anilino-group in amino-alcohols derived fro aniline and its homologues was investigated. The aromatic ami was made to react with epichlorohydrin, and the derivative th obtained treated with dimethylamine or one of its homologues.

The following substances are described: *α*-p-*phenetidino-γ-dimethylaminoisopropyl alcohol*,

$$EtO{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NMe_2,$$

b. p. 212°/14 mm., m. p. 79°; *α*-p-*toluidino-γ-dimethylaminoisopropyl alcohol*, $C_6H_4Me{\cdot}NH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NMe_2$, b. p. 190° 12 mm., m. p. 72°; *α-methylanilino-γ-dimethylaminoisopropyl alcohol*, $NMePh{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NMe_2$, b. p. 168°/14 mm. *α-anilino-γ-dimethylaminoisopropyl alcohol*, b. p. 195°/21 mm m. p. 84°; *α-ethylanilino-γ-dimethylaminoisopropyl alcohol*, b. p 195°/15 mm.; *α*-m-*nitroanilino-γ-dimethylaminoisopropyl alcoho* m. p. 95°; and *α*-o-*anisidino-γ-dimethylaminoisopropyl alcoho* b. p. 198—200°/30 mm.

The anæsthetic action of benzoylmethylanilinodimethylamin *iso*propyl alcohol hydrochloride is slower than that of stovaine total anæsthesia is obtained in twenty minutes with *N*/50-solution and in seventeen minutes with *N*/25-solutions; *N*/25-stovain solutions, on the other hand, act in four to five minutes.

W. R. S.

The Hydrobenzoin Transposition. Influence of th Nature of the Reagent. M. Tiffeneau and A. Orékhoff (*Compt rend.*, 1920, **171**, 400—402. Compare Tiffeneau and Dorlencour A., 1906, i, 724; Orékhoff, A., 1919, i, 272).—With the exception c *αββ*-triphenylethanediol, which is really an aryl hydrobenzoin, th dehydration of the alkylhydrobenzoins may take place in severa different ways, depending on the concentration of the sulphuri acid used and the nature of the alkyl group.

Thus, with dilute sulphuric acid, *αβ*-diphenylbutane-*αβ*-dio yields *αα*-diphenylbutaldehyde, but with concentrated sulphuri acid it gives ethyldeoxybenzoin and diphenylmethyl ethyl keton *αβ*-Diphenylpropane-*αβ*-diol, on the other hand, only yields methy deoxybenzoin with concentrated sulphuric acid. W. G.

The Hydrobenzoin Transposition. Influence of the p-Methoxyl Substitution on the Dehydration of Triarylethanediols. A. Orékhoff and M. Tiffeneau (*Compt. rend.*, 1920, **171**, 473—476).—Under the influence of the same dehydrating agent, the triarylethanediols undergo change with or without molecular transposition. When the secondary alcohol group is attached to the same carbon atom as a phenyl group, there is no transposition, a ketone being formed. If the phenyl group is replaced by an anisyl group, there is transposition, with the formation sometimes of a single compound, a triarylacetaldehyde, the anisyl group migrating, sometimes with the formation of two compounds, the aldehyde and a ketone, in which case the phenyl group migrates. These reactions, simple and mixed, depend on the position of the hydroxyl group eliminated, and the stability of the hydroxyl groups appears to depend on the nature of the substituent groups. Thus αβ-dianisyl-α-phenylethanediol yields *pp'*-dimethoxytriphenylacetaldehyde, $(C_6H_4{\cdot}OMe)_2CPh{\cdot}CHO$, whilst αα-diphenyl-β-anisylethanediol yields *p*-methoxytriphenylacetaldehyde,

$$OMe{\cdot}C_6H_4{\cdot}CPh_2{\cdot}CHO,$$

and phenyl *p*-methoxydiphenylmethyl ketone,

$$OMe{\cdot}C_6H_4{\cdot}CHPh{\cdot}COPh.$$

W. G.

Preparation of Mercury Compounds of Sulphophenolcarboxylic Acids and their Homologues which yield Colloidal Solutions with Water. Saccharin-Fabrik Aktien-Gesellschaft vorm. Fahlberg List & Co. (D.R.-P. 321700; from *Chem. Zentr.*, 1920, iv, 292).—(i) The mercuration of the sulphocarboxylic acids is effected in acid solution. (ii) The solutions of sulphophenolcarboxylic acids or their homologues are warmed or allowed to remain in contact with solutions of mercury salts, or the aqueous solutions of the sulphocarboxylic acids are similarly treated with an amount of mercuric oxide insufficient for the saturation of the three acidic groups (less than 1·5 molecules of oxide for each molecule of sulphophenolcarboxylic acid). Alternatively, the mercury compounds of the sulphophenolcarboxylic acids, which are sparingly soluble or insoluble in water, are warmed with acids or mixtures or compounds containing mercury and salicylic acid, or its homologues are treated at the ordinary or elevated temperature with concentrated sulphuric acid, and subsequently with a dilute acid. *Mercurisulphosalicylic acid* (from 5-sulphosalicylic acid) and *mercurisulpho*-m-*cresotic acid* form colourless crystals, very sparingly soluble in organic media, readily soluble in water to colloidal, viscous solutions. H. W.

Reduction of *o*-**Benzoicsulphinide** [**"Saccharin"**]. F. Gianformaggio (*Gazzetta*, 1920, **50**, i, 327—340).—Previous investigations on reduction by means of amyl alcohol and sodium have been confined more especially to *o*-phenolcarboxylic acids, with which the benzene nucleus undergoes rupture between the hydroxyl and carboxyl groups, acids of the pimelic acid series being produced, and to *m*-phenolcarboxylic and *o*- and *p*-amino-

benzoic acids, which are reduced without rupture of the benzer ring.

In the reduction of *o*-benzoicsulphinide by means of sodiu and amyl alcohol, the nascent hydrogen formed eliminates th *imino-group* as ammonia, and also detaches the sulphonic grou which, after acidification, is liberated as sulphur dioxide; the fin product of the reaction is hexahydrobenzoic acid, *o*-sulphobenzo acid being probably formed as an intermediate product.

Of the various secondary products formed in reductions by mea of sodium and amyl alcohol, owing to reactions between the alcoh and its sodium derivative (compare Einhorn and Lumsden, A 1896, i, 45; Guerbet, A., 1899, i, 472), the author has identifie only valeric acid.

A basic compound, which distils in a current of steam, is al formed in small proportion during the reduction of *o*-benzoi sulphinide, and is to be investigated further. T. H. P.

Action of Acetic Anhydride on *a*-Naphthylpropiolic Acid BYRON L. WEST (*J. Amer. Chem. Soc.*, 1920, **42**, 1656—1669).— When heated with potassium cyanide, sodium naphthalene-c sulphonate gave *a*-naphthonitrile, from which *a*-naphthoamide wa prepared. The latter, when reduced in alcoholic hydrochloric aci with sodium amalgam, gave *a*-naphthylmethyl alcohol, which wa readily oxidised to *a*-naphthaldehyde. This aldehyde, when treate with malonic acid in the presence of alcoholic ammonia and sub sequent addition of acid, gave a mixture of two acids, which, o heating, yielded *a-naphthylacrylic acid*, m. p. 207·5°, giving a *ethyl* ester. On bromination, the ester gave *ethyl aβ-dibromo β-1-naphthylpropionate*, $C_{10}H_7$·CHBr·CHBr·CO_2Et, which, wit alcoholic potassium hydroxide, yielded *a-naphthylpropiolic acid* $C_{10}H_7$·C:C·CO_2H, m. p. 134—135°, giving a *potassium* salt.

When heated with acetic anhydride, *a*-naphthylpropiolic acid yielded 8-*a-naphthylphenanthrene*-6:7-*dicarboxylic anhydride*, m. p 207—209° (compare Michael and Bucher, A., 1898, i, 256), from which a very insoluble *sodium* salt was prepared. The anhydride gave Baeyer's phthalein reaction and fluorescein test. W. G.

Preparation and Properties of Cellulose Phthalate. H. A. LEVEY (*J. Ind. Eng. Chem.*, 1920, **12**, 743—744).—Cellulose phthalate, $C_8H_4O_3,8C_6H_{10}O_5,4H_2O$, was prepared by heating cotton cellulose (previously converted into "hydrocellulose" by treatment with a solution of chlorine in glacial acetic acid) for twenty-four hours at 70° with phthalic anhydride and zinc chloride in the minimum quantity of ethyl phthalate (or acetic acid), washing the resulting ester, and drying it not above 70° in a vacuum. The cellulose phthalate thus obtained was insoluble in alcohol, ether, acetic acid, ethyl phthalate, and other ordinary solvents. The presence of zinc chloride or other condensing agent is essential for the esterification. Phthalic anhydride does not displace the acetate radicle from cellulose acetate or the nitrate radicle from cellulose nitrate, even when the zinc chloride is replaced by sulphuric acid.
C. A. M.

Catalytic Hydrogenation of Cholesterol and Cholesterylene. F. F. NORD (*Biochem. Zeitsch.*, 1919, **99**, 261—267).—Cholesterol in acetone solution was reduced by hydrogen in the presence of colloidal palladium until no more of the gas was absorbed. The dihydrocholesterol, $C_{27}H_{48}O$, produced, m. p. 141°, formed an acetyl derivative, m. p. 110°. Cholesterylene was hydrogenised in the same way, and yielded cholestane, b. p. 269—271°/12 mm., $[\alpha]_D^{15}$ +43·32°. S. S. Z.

Action of Alcoholic Sodium Acetate Solution on Cholesterol Dibromide. A. WINDAUS and H. LÜDERS (*Zeitsch. physiol. Chem.*, 1920, **109**, 183—185).—The authors have prepared the so-called metacholesterol described by Lifschütz (A., 1919, i, 591), and find that: (1) it yields ordinary cholesterol dibromide, reduction of which gives cholesterol, m. p. 146°; (2) its melting point is raised from 141—142° to 145° by repeated crystallisation from methyl alcohol; (3) the *iso*butyrate and acetate are identical with those prepared from cholesterol. The conclusion is drawn that "metacholesterol" consists principally of ordinary cholesterol. T. H. P.

Isomerism in the Series of Aromatic α-Ketonic Acids. H. GAULT and R. WEICK (*Compt. rend.*, 1920, **171**, 395—398).—It has previously been shown (this vol., i, 485) that ethyl phenylpyruvate can be obtained in two isomeric forms, *α*-, m. p. 51°, and *β*-, b. p. 149°/15 mm. A third isomeride, γ-, m. p. 79°, has now been obtained by the action of sodium acetate on the *β*-isomeride. The constitutions assigned to these three isomerides are:

$$\begin{array}{ccc} \begin{array}{c} H\cdot C\cdot Ph \\ \| \\ HO\cdot C\cdot CO_2Et \end{array} & \begin{array}{c} Ph\cdot C\cdot H \\ \| \\ HO\cdot C\cdot CO_2Et \end{array} & CH_2Ph\cdot CO\cdot CO_2Et \\ \alpha. & \beta. & \gamma. \end{array}$$

It is shown that the *α*- and *β*-isomerides, when brominated in carbon disulphide solution at −15°, give a *dibromo*-derivative, $CHPhBr\cdot CBr(OH)\cdot CO_2Et$, m. p. 55—60°, which decomposes very rapidly at the ordinary temperature, losing hydrogen bromide and giving the *compound*, $CHPhBr\cdot CO\cdot CO_2Et$, b. p. 184°/20 mm. The γ-isomeride is only brominated in boiling carbon disulphide, and gives *ethyl β-bromo-α-keto-β-phenyl-γ-benzylbutyrolactone-γ-carboxylate*, $CO<\begin{array}{l} O—C(CO_2Et)\cdot CH_2Ph \\ CO\cdot CPhBr \end{array}$, m. p. 151°.

The *α*- and γ-esters are converted into the *β*-ester by slow distillation under reduced pressure. The *β*- and γ-esters are converted into the *α*-ester by shaking in ethereal solution with sodium carbonate, whilst the *β*-ester is converted into the γ-ester, as described above. W. G.

Preparation of Aldehydes and Ketones. CARL HARRIES (D.R.-P. 321567; from *Chem. Zentr.*, 1920, iv, 292).—Ozonides are treated with reducing agents, particularly with potassium ferrocyanide, in the presence or absence of acids, whereby the formation of resins is considerably restricted. The solution of *iso*eugenol ozonide in ethyl acetate gives vanillin in 95% yield.

n-Oleic acid ozonide gives nonaldehyde. The ozonides from ta oil, gas oil, and the unsaturated oils, obtained by chlorination o crude paraffin and elimination of hydrogen chloride, yield mainl aldehydes in addition to ketones and small amounts of acids.

H. W.

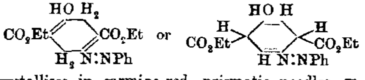
Manufacture of Protocatechualdehyde. CONFECTIONERY INGREDIENTS, LTD., FRANCIS EDWARD MATTHEWS, ALBERT THEODORE KING, and THOMAS KANE (Brit. Pat. 145871).—The acid chloride of any suitable acyl derivative of protocatechuic acid such as the diacetate, dibenzoate, carbonate, or di-*p*-toluene sulphonate, or of the dibenzyl ether of protocatechuic acid, is reduced to the corresponding derivative of protocatechualdehyde by treatment in an inert solvent at boiling temperature with hydrogen in presence of a hydrogenating catalyst, such as palladium or nickel. When the evolution of hydrogen chloride ceases, the reduction product is hydrolysed and protocatechualdehyde isolated as its bisulphite compound in the usual way. G. F. M.

Perfumes from Perillaldehyde. S. FURUKAWA (Jap. Pat 35332).—An alcoholic solution of the aldehyde (150 grams in 500 c.c.) is heated for two hours on the water-bath with hydroxyl amine hydrochloride (70 grams) and sodium hydrogen carbonate (100 grams). The resulting oxime, m. p. 102°, is two thousand times as sweet as sucrose; it is easily converted into perillonitrile b. p. 116—118°/11 mm., D^{15} 0·94—0·949, which is two hundred times as sweet as sucrose, and is suitable as an ingredient of tooth powders or perfumes. CHEMICAL ABSTRACTS.

The Isomerism of the Oximes. IX. 2 : 4-Dinitrobenz aldoxime and Bromo-substituted Hydroxy- and Methoxy benzaldoximes. VERA WENTWORTH and OSCAR LISLE BRADY (T. 1920, **117**, 1040—1045).

Unsaturated Compounds in Organic Chemistry. II Constitution of Succinylsuccinic Ester. M. GIUA (*Gazzetta* 1920, **50**, i, 387—393).—The action of phenylhydrazine and o *as*-phenylmethylhydrazine on ethyl succinylsuccinate has been investigated (compare Knorr and Bülow, A., 1884, 1380; von Baeyer, Jay, and Jackson, A., 1891, 1486; von Baeyer and von Brüning, A., 1891, 1486; Kijner, A., 1894, i, 67).

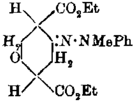
The action of phenylhydrazine (1 mol.) on ethyl succinyl succinate (1 mol.) in alcoholic solution and in presence of aceti acid yields (1), as principal product, the *compound*,



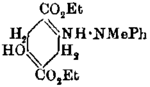
which crystallises in carmine-red, prismatic needles, m. p. 142° dissolves in sulphuric acid to a colourless solution, and is only slowly attacked by boiling concentrated alkali solution. Reduction of this compound by means of sodium and alcohol yields a viole

compound, which does not melt at 240° and dissolves in alkali solution with yellow coloration. (2) Ethyl benzenedihydrazodihydroterephthalate, m. p. 204—205° (compare Knorr, *loc. cit.*, von Baeyer, *loc. cit.*). The latter and its isomeride, m. p. 166° form the principal products of the reaction when 2 mols. of phenylhydrazine are taken per 1 mol. of the succinylsuccinic ester. Whatever the proportions between the reacting compounds, the reaction yields always a viscous, tar-like resin, which partly decomposes, with formation of aniline, when distilled under a pressure of 52 mm.

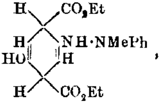
The action of *as*-phenylmethylhydrazine on ethyl succinylsuccinate in alcoholic solution containing acetic acid yields the *compound*,



or, more probably,



or



which crystallises in golden-yellow needles, m. p. 135—136°, and dissolves in concentrated sulphuric acid, giving a reddish-yellow solution.
T. H. P.

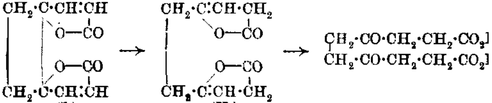
Manufacture of Aromatic Alkylamino-compounds [Alkylaminoanthraquinones]. FREDERICK WILLIAM ATACK and WALTER NORMAN HAWORTH (Brit. Pat. 147964).—The aminoanthraquinones are alkylated by treatment with an alkyl sulphate in solution in a neutral medium of high boiling point, such as nitrobenzene or tetrachloroethane, in presence of a mild alkali, such as sodium carbonate. Thus 20 parts of 1-aminoanthraquinone may be dissolved in 216 parts of nitrobenzene and 20 parts of sodium carbonate added, the mixture being heated to boiling under a reflux condenser, while 17½ parts of methyl sulphate are added during the space of two hours. A yield of 87% of 1-methylaminoanthraquinone is obtained. When 5 parts of 2-aminoanthraquinone are similarly treated with 6 parts of methyl sulphate 2-*dimethylaminoanthraquinone is the chief product.* G. F. M.

Rhinanthocyanin. A. NESTLER (*Ber. deut. bot. Ges.*, 1920, 38 117—121).—When rhinanthin is extracted from the seeds of *Alectorolophus hirsutus* by means of 70% alcohol containing 5% of hydrochloric acid, the glucoside is gradually hydrolysed by the acid into a blue colouring matter, rhinanthocyanin, and a sugar. This hydrolysis may be effected also, although less rapidly, by sulphuric

oxalic, citric, lactic, or acetic acid, and the production of t so-called blue (mostly dark brownish-violet) bread is due to cc tamination of the flour with the meal of seeds containing rhinanth and hydrolysis of the latter by means of the lactic acid form during the fermentation. In the course of a few hours or da the blue rhinanthocyanin solution becomes colourless and depos blue or green granules, which sometimes retain their colour f many weeks, and sometimes turn brown. Rhinanthocyanin impa a blue or green coloration to chloroform, but does not dissol therein; the colour is due to the presence of granules, 0·7—1 μ size, and of droplets of 2·5—7 μ, and is removable by ult filtration. T. H. P.

Chitin and Chitin Derivatives of Animal and Plant Origi O. Schmiedeberg (*Arch. expt. Path. Pharm.*, 1920, **87**, 74—8(—Chitin was prepared by dissolving moulds, previously freed frc cellulose, in concentrated hydrochloric acid and filtering; the chit was then precipitated from the filtrate by the addition of wat and washed until free from chloride. From the elementa analysis, the formula $C_{34}H_{56}O_{22}N_4$ was calculated, which sugge that the chitin lost one acetyl group in the treatment with hyd chloric acid. It seems to resemble chitin of animal origiu, wi the exception that it is less resistant to the action of acids a alkalis. A compound resembling Winterstein's paradextr was prepared by the author from mould cellulose. The work previous investigators on chitin is reviewed. S. S. Z.

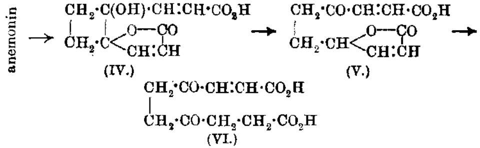
Transformations of Anemonin by Acids and Alkalis. V Y. Asahina and A. Fujita (*J. Pharm. Soc. Japan*, 1920, No. 46 Compare A., 1892, i, 241; 1896, i, 623; 1899, i, 930; 1914, i, 56 1915, i, 1067; 1916, i, 401; this vol., i, 70, 321, 493).—Havi settled the constitution of anemonin (I) by synthesis (this vo i, 493), the authors now explain its transformations. Co sulphuric acid is without actiou; the hot, dilute acid changes it anemoninic acid (VI). Cold concentrated hydriodic acid dissolv the substance, and, on keeping, anemonolic acid (III) separat quantitatively, probably after intermediate formation of dihydr anemonin (II).



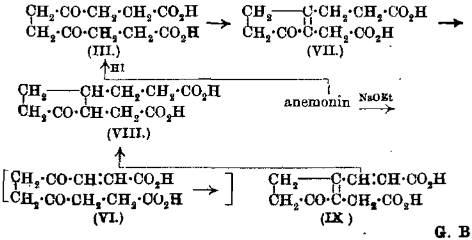
(I.) (II.) (III.)

When warmed with methylsulphuric acid, anemonin yields th *methyl* ester, $C_{12}H_{14}O_5$, m. p. 62°, of furan-2-propionic-5-acryl acid, m. p. 179°. This acid is reduced by sodium amalgam t furan-2:5-dipropionic acid, which is also formed by prolonged hea ing of anemonolic acid above its melting point. The authors ca not confirm the higher melting point of furan-2-propionic-5-acryl acid, given by Cooper and Nuttall (T., 1914, **105**, 2218).

Concentrated potassium carbonate solution changes anemonin into anemoninic acid (VI), which can be isolated in a 10% yield as crystals of the α-variety, m. p. 117°. This is readily transformed by concentrated hydrochloric acid at 60° to the β-variety, m. p. 189°. The two forms are probably *cis-trans*-modifications. Both yield with ammonia an impure pyrrole derivative. The β-acid yields with concentrated sulphuric acid and methyl alcohol its own methyl ester, m. p. 128°, together with that of furan-2-propionic-5-acrylic acid (above). Anemoninic acid is oxidised by permanganate to acetonediacetic (γ-ketopimelic) acid. The formation of anemoninic acid (VI) from anemonin is represented as follows; IV and V are hypothetical:



Sodium and 98% alcohol transform anemonin into α-anemonic acid (IX), m. p. 120°, which is changed by heating with concentrated hydrochloric acid to the stereoisomeric β-variety, m. p. 210°. Both are reduced catalytically to the same tetrahydroanemonic acid (VIII), m. p. 135°. Anemonolic acid (III) is transformed by alcoholic potassium hydroxide at the ordinary temperature to *anhydroanemonolic acid* (VII), $C_{10}H_{12}O_5$, m. p. 129°, yielding a *semicarbazone*, m. p. 208°. This acid combines with one molecule of hydrogen catalytically, and is then found to be identical with tetrahydroanemonic acid (VIII), formed by reduction of anemonic acid, whence the constitution IX is deduced for the latter. Its formation from anemonin by sodium ethoxide is attributed to the intermediate formation of anemoninic acid (VI), although the latter itself could not be converted into anemonic acid.



G. B.

Nature of the Red Dye of Crustaceæ. J. VERNE (*Compt. rend. Soc. Biol.*, 1920, **83**, 963—964; from *Chem. Zentr.*, 1920, iii, 259).—The red dye of crustaceæ behaves in the same manner as carotin towards solvents. The latter also yields a violet-brown additive compound with iodine and a blue coloration with sulphuric acid. The absorption bands of both dyes are similar. The dye of the crustaceæ is a compound with carbon and hydrogen in the ratio 5:7, and, according to ebullioscopic determinations, has the empirical formula $C_{40}H_{56}$. H. W.

A Comparative Study in the Xanthone Series. I. SURENDRA NATH DHAR (T., 1920, **117**, 1053—1070).

Preparation of Derivatives of Hydrastinine. KARL W. ROSENMUND (D.R.-P. 320480; from *Chem. Zentr.*, 1920, iv, 223). —The process depends on (i) the treatment of methylenedioxyphenyl*iso*propylamine with formaldehyde or substances which yield formaldehyde and catalytically active agents, and oxidation of the condensation product thus formed; (ii) the condensation of methylenedioxyphenyl*iso*propylamine with formaldehyde or substances which yield formaldehyde, transformation of the alkylideneamine thus produced with the aid of active catalysts, alkylation, and oxidation of the substance so formed; (iii) the use of iodine as oxidising agent. 6:7-Methylenedioxy-3-methyltetrahydro*iso*quinoline, m. p. 65—67°, is obtained by heating the oily product of the action of calculated quantities of methylenedioxyphenyl*iso*propylamine and formaldehyde with hydrochloric acid (25%) at 100°. The base is converted by methyl iodide into *3-methyldihydrohydrastinine hydriodide*, m. p. 240°; the free *base* has m. p. 86°, whilst the *hydrochloride* has m. p. 230°. The hydrochloride is directly obtained when methylenedioxyphenyl*iso*propylamine hydrochloride (1 part) and commercial formaldehyde solution (2 parts) are heated for three hours at 130—135°. 3-Methyldihydrohydrastinine is converted by iodine and potassium acetate in alcoholic solution into *3-methylhydrastinine hydriodide*, m. p. 207° (*base*, m. p. 103—104°). The *dichromate*, obtained by the action of potassium dichromate and sulphuric acid on an aqueous solution of 3-methyldihydrohydrastinine hydrochloride, is oily. *3-Methyl-*N*-ethyldihydronorhydrastinine hydriodide* separates on boiling a solution of 3-methyldihydronorhydrastinine in benzene, and is oxidised to *3-methyl-*N*-ethylnorhydrastinine* (*hydriodide*, yellow crystals, m. p. 210°). The products are less toxic than hydrastinine. H. W.

Preparation of Tropinonecarboxylic Esters. R. WILLSTÄTTER (D.R.-P. 302401; from *Chem. Zentr.*, 1920, iv, 42—43).—*N*-Methylpyrrolidinediacetic esters are treated with an alkali metal or other condensing agent. The initial material for the synthesis is succinyldiacetic ester, which is transformed by methylamine in

acetic acid solution, for example, into the corresponding *N*-methylpyrrolediacetic ester; the latter is reduced by hydrogen in the presence of platinum in acetic acid solution to *N*-methylpyrrolidinediacetic ester. The diethyl ester is a colourless, mobile oil with an alkaline reaction, b. p. 162·5°/9 mm., whilst the methyl ester has b. p. 155·5°/12 mm. The *N*-methylpyrrolidinediacetic esters lose alcohol under the influence of sodium, sodium alkoxides, or sodamide, and yield tropinonecarboxylic esters,

$$\begin{array}{l} CH_2\cdot CH\cdot CH_2\cdot CO_2Et \\ \mid \quad \quad >NMe \\ CH_2\cdot CH\cdot CH_2\cdot CO_2Et \end{array} \longrightarrow \begin{array}{l} CH_2\cdot CH \text{———} CH\cdot CO_2Et \\ \mid \quad \quad >NMe \quad >CO \\ CH_2\cdot CH \text{———} CH_2 \end{array} .$$

For further preparations, the ester is only obtained in solution or mixed with sodium salts; its separation from admixture with organic substances is difficult, since it is very readily decomposed and resinified; it is very slightly soluble in water and exhibits a strong ferric chloride reaction. Ethyl tropinonecarboxylate is converted by warm dilute acid into tropinone, which can be isolated in substance or as the picrate or dibenzylidene derivative; it is reduced electrolytically or by sodium amalgam to *r*-ecgonine ester.

H. W.

Heterocyclic Compounds of *N*-Arylamino-alcohols. R. E. Rindfusz and V. L. Harnack (*J. Amer. Chem. Soc.*, 1920, **42**, 1720—1725).—Aniline condenses with trimethylene chlorohydrin to give *γ-hydroxypropylaniline*, $NHPh\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, b. p. 192°/30 mm., n^{20} 1·502, D^{20} 1·063, and *di-γ-hydroxypropylaniline*, $NPh(CH_2\cdot CH_2\cdot CH_2\cdot OH)_2$, b. p. 241—242°/25 mm., n^{24} 1·565, D^{26} 1·097. When dehydrated by phosphoric oxide, the first-named compound yields tetrahydroquinoline, whilst the second yields julolidine. Tetrahydroquinoline, when condensed with allyl bromide, gives 1-*allyltetrahydroquinoline*, b. p. 135°/25 mm., n^{24} 1·556, D^{24} 1·024, and with trimethylene chlorohydrin gives 1-*γ-hydroxypropyltetrahydroquinoline*, b. p. 227—229°/18 mm., n^{31} 1·561, D^{27} 1·091, which, on dehydration, yields julolidine.

β-Hydroxyethylaniline, $NHPh\cdot CH_2\cdot CH_2\cdot OH$, has b. p. 188°/30 mm., n^{24} 1·576, D^{24} 1·101, and *di-β-hydroxyethylaniline*,

$$NPh(CH_2\cdot CH_2\cdot OH)_2,$$

has b. p. 228°/15 mm., m. p. 53·5—54°. *β*-Hydroxyethylaniline on dehydration gives diphenylpiperazine, and di-*β*-hydroxyethylaniline yields phenylmorpholin.

W. G.

The Cyanine Dyes. II. The Synthesis of *o*-Aminocinnamylidenequinaldine Methiodide. William Hobson Mills and Percy Edwin Evans (T., 1920, **117**, 1035—1040).

Thiocyanates and Thiocarbimides. XIV. A New Method of Synthesising 2-Thiohydantoins. Treat B. Johnson, Arthur J. Hill, and Erwin B. Kelsey (*J. Amer. Chem. Soc.*, 1920, **42**, 1711—1720).—*ω*-Aminoacetanilide reacted with carbon disulphide

in alcoholic solution to give the unstable *ω-aminoacetanilide* salt of the corresponding dithiocarbamic acid,

$NHPh{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}SH,NH_2{\cdot}CH_2{\cdot}CO{\cdot}NHPh$,

m. p. 145° (*decomp.*), which, by the action of ethyl chloroformate, was converted into the *carbethoxy*-derivative,

$NHPh{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}S{\cdot}CO_2Et$,

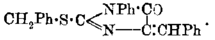
and this, on distillation, yielded 2-thio-1-phenylhydantoin. This thiohydantoin, when digested with chloroacetic acid, was converted into 1-phenylhydantoin.

When ethyl chloroformate acted directly on ω-aminoacetanilide, *ω-carbethoxyaminoacetanilide*, m. p. 137·5°, was obtained, which was converted by the action of alcoholic potassium hydroxide into 1-phenylhydantoin.

The dithiocarbamate (above), when digested with mercuric chloride, was converted into ω-thiocarbimidoacetanilide,

$NHPh{\cdot}CO{\cdot}CH_2{\cdot}NCS$,

which spontaneously and immediately condensed to give 2-thio-1-phenylhydantoin, the benzylidene derivative of which condensed with benzyl chloride in the presence of sodium ethoxide to give *2-benzylthiol-1-phenyl-4-benzylidenehydantoin*,



m. p. 178°.

The spontaneous change of the thiocarbimide,

$NHPh{\cdot}CO{\cdot}CH_2{\cdot}NCS$,

into 2-thio-1-phenylhydantoin, and the series of changes described above, are taken as strong snpport of the view that the conversion of compounds of the type $NHR{\cdot}CO{\cdot}CH_2Cl$ into ψ-thiohydantoins, is by passage through the normal thiocyanate (A., 1918, i, 256), and not through the thiocarbimide (Beckurts and Frerichs, A., 1915, i, 798, 799). W. G.

Preparation of Isatin and its Substitution Products. J. R. Geigy (D.R.-P. 320647; from *Chem. Zentr.*, 1920, iv, 223).—ω-Oximinoacetanilide, $NHPh{\cdot}CO{\cdot}CH{:}N{\cdot}OH$, or its halogen, alkyl, alkyloxy-, or carboxyl substitution products, which are capable of condensation, are warmed with concentrated sulphuric acid, and the isatinimines, of the general formula $R{<}{}^{NR'}_{C(:NH)}{>}CO$ (in which R represents a substituted or unsubstituted benzene nucleus and R′ a hydrogen, alkyl, or arylalkyl group), which are thus formed are decomposed by water into isatins and ammonia. The following examples are cited: isatin from ω-oximinoacetanilide; 5-methylisatin from ω-oximinoaceto-*p*-toluidide; *4-chloro-7-methoxyisatin*, m. p. 240°, from chloro-ω-oximinoacetanisidide; *isatin-7-carboxylic acid*, m. p. 235°, from ω-oximinoacetylanthranilic acid; 5-chloroisatin from *p*-chloro-ω-oximinoacetanilide; 4:7-*dichloroisatin*, orange-yellow crystals, from 2:5-dichloro-ω-oximinoacetanilide; *N*-ethyl-ψ-isatin, dark red crystals, from ω-oximinoaceto-

ethylanilide; *N*-benzyl-ψ-isatin, orange-yellow substance, from ψ-oximinoacetobenzylanilide. H. W.

Changes in the Physical State of Colloids. XXIII. Acid-albumin. Mona Adolf and Ernst Spiegel (*Biochem. Zeitsch.*, 1920, **104**, 175—189).—In the conversion of serum-albumin into acid-albumin by the action of boiling hydrochloric acid, the protein molecule changes in its acid-combining, but not in its alkali-combining, power. One gram of acid-albumin combines at most with 2·5 millimols. of sodium hydroxide, the equivalent weight of the acid-albumin being thus 416, which is the value found for the natural serum-albumin. The acid-combining power of acid-albumin is, however, 20% higher than that of the albumin itself. The values for the viscosity of acid-albumin solution are higher than those of the protein, but they exhibit the same changes on addition of acid or alkali, these changes being hence due to similar ionisation influences.

On addition of alkali hydroxide or acid to a solution of the natural albumin, the rotatory power reaches a maximum corresponding with the maximum of acid or alkali-combining power, this maximum persisting even when the excess acidity for a 1% solution amounts to 0·1*N*. When hydrochloric acid is added to an acid-albumin solution, the rotatory power changes and shows a distinct maximum at 0·058*N*-acidity, but diminishes at higher acidities; the maximum rotation corresponds, not with the maximum of ionisation indicated by the viscosity curve, but with an appreciably higher acidity. According to conductivity measurements, acid-albumin in neutral salts is tervalent, the velocity of migration being $V = 41·1$.

Addition of salts of the heavy metals precipitates acid-albumin when dissolved in sodium hydroxide solution, but not when dissolved in hydrochloric acid; this precipitation hence represents a reaction only for the negative protein ion. T. H. P.

Changes in the Physical State of Colloids. XXIV. Precipitation of Protein by Acids and Alkalis. Richard Wagner (*Biochem. Zeitsch.*, 1920, **104**, 190—199. Compare Pauli and Handovsky, A., 1909, i, 618; Pauli and Wagner, A., 1910, ii, 830).—Results are given of investigations on (1) the concentrations of a number of different acids just sufficient to produce flocculation in serum-albumin, (2) the viscosities of serum-albumin containing various acids in the concentration 0·05*N*, and (3) the swelling of glutin in 0·05*N*-acid. From these results, the conclusions are drawn that the state of the protein salt, as regards hydration and ionisation, conditions the precipitability of this salt in excess of acid, and that there is no reason to suppose that this precipitability is not primarily to be considered as displacement of a salt from solution by excess of its acid.

According to the author's views on the mode of salt-formation between alkali and protein, relations similar to the above should

hold in this case, and this is actually found with pure serum-albumin and alkali hydroxide in concentrations exceeding 5*N*.

T. H. P.

Some Properties of Serin. M. PIETTRE and A. VILA (*Compt. rend.*, 1920, **171**, 371—373).—Serin, as prepared from the serum of horse blood by the method previously described (*ibid.*, 170), is soluble in water even after drying at 40° or in a vacuum over sulphuric acid. It has $[\alpha]_D$ $-57°$ to $-58°$, and contains much higher percentages of sulphur and calcium than the corresponding serum globulin. It exhibits the property of separating from its solution in an almost solid, granular mass at 0°, and dissolving again at the ordinary temperature.

W. G.

Changes in the Physical Condition of Colloids. XXII. The General Chemistry of the Caseinates. II. WOLFGANG PAULI and JOHANN MATULA (*Biochem. Zeitsch.*, 1919, **99**, 219—236. Compare Pauli, A., 1915, i, 1016).—Conductivity experiments show that there are two zones in the reaction of casein with alkali hydroxide. In one zone, in which the reaction is neutral, the valency of the caseinate ions remains constant, whilst the conductivity increases slightly. In the second zone, when more alkali is added, both the valency and the conductivity of the caseinate ions increase. It is deduced from the conductivity curves that there exists a neutral tribasic caseinate which can take up more caseinogen without changing its valency.

S. S. Z.

Causes of the Conductivity of Casein Solutions. L. MÁNDOKI and M. POLÁNYI (*Biochem. Zeitsch.*, 1920, **104**, 254—258).—Measurements of the electrical conductivity of neutral casein solutions show that the protein in solution is not a good conductor, so that the conductivity of these solutions must be due largely to decomposition products of the casein (compare Laqueur and Sackur, A., 1903, i, 300; Robertson, "Physical Chemistry of the Proteins").

T. H. P.

Benzene Derivatives in Glutin and Protein-content of Gelatin. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1920, **109**, 32—48. Compare A., 1919, i, 502).—The author has investigated the benzene derivatives formed when the best commercial gelatin is subjected in solution at 40° to the action of a maceration of putrefying meat in presence of potassium dihydrogen phosphate, magnesium sulphate, sodium carbonate, and, in some cases, sodium potassium tartrate. The products identified comprise: (1) Traces of an indole derivative. (2) About 0·11% of aromatic hydroxy-acids, calculated on the anhydrous, ash-free material, indicating that gelatin contains the tyrosine group in appreciable proportion; succinic acid, derived from the aspartic acid of the gelatin, is also

found in small quantity. (3) At least 1·3% of phenylpropionic acid. It has also been found possible to isolate a protein from gelatin.

T. H. P.

Prosthetic Group of Blood Pigment. Action of Diazomethane on certain Colouring Matters and on Anhydrous Ferric Chloride. William Küster (*Zeitsch. physiol. Chem.*, 1920, **109**, 108—116).—According to the ordinary formula for hæmin, the chlorine is assumed to be united to iron, although union with nitrogen is not excluded. In the action of diazomethane on different hæmins showing marked differences as regards esterification, removal of the halogen has never been observed. The author [with O. Kusch] has now investigated the action of diazomethane on the hydrochlorides of various colouring matters of known constitution, and also on anhydrous ferric chloride. The results obtained indicate that true hæmins are allied rather to this anhydrous chloride, which is altered but little by diazomethane, than to the hydrochlorides of di- and tri-phenylmethane dyes, from which hydrogen chloride is very easily withdrawn, with formation of methyl chloride. With the hydrochloride of a furylmethylindolenylmethane, the reaction is less ready, and with crystal-violet reduction to the leuco-base takes place. Finally, with a rhodamine hydrochloride no esterification occurs, so that the carboxyl group cannot be free, and an oxonium grouping must be assumed (compare Noelting and Dziewoński A., 1905, i, 935).

The action of diazomethane on *Pyoctaninum coeruleum*, that is, on pentamethyltriaminotriphenylmethyl chloride,

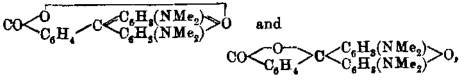
$$NHMe\cdot C_6H_4\cdot CCl(C_6H_4\cdot NMe_2)_2,$$

results in removal of 86·7% of the halogen. With *P. aureum*, that is, tetramethyldiaminodiphenylaminomethyl chloride,

$$NH_2\cdot CCl(C_6H_4\cdot NMe_2)_2,$$

79·2% of the chlorine is withdrawn.

Tetramethylrhodamine hydrochloride, $C_{24}H_{23}O_3N_2Cl$, obtained from dimethyl-*m*-aminophenol and phthalic anhydride, forms green plates with metallic lustre, m. p. (dry) 288—290°, and dissolves in water or alcohol, giving a carmine-red solution showing orange-yellow fluorescence. The free base is obtained in green leaflets exhibiting metallic lustre, and dissolves sparingly in ether or light petroleum, and more readily in benzene, toluene, or xylene, giving colourless solutions. The constitutions of the coloured and colourless modifications of the base are



respectively. In benzene solution, the anhydrous base is unaltered by diazomethane, which, however, withdraws 97·4% of the chlorine from the hydrochloride, but does not esterify the base. The *methyl ester* of tetramethylrhodamine, $C_{25}H_{26}O_4N_2$, obtained by passing

hydrogen chloride into a solution of the hydrochloride in methyl alcohol, forms violet-red needles, m. p. 190°, is insoluble in 5% sodium carbonate solution at the ordinary temperature, but dissolves, with hydrolysis, in cold 1% sodium hydroxide solution, giving a red solution; it is soluble also in hydrochloric acid with a red coloration.

Furyl-α-methylindolenylmethane hydrochloride,

$$\left[C_6H_4\begin{matrix}\diagup C{:}CH{\cdot}C_4H_3O \\ \diagdown NH{:}\overset{|}{C}Me\end{matrix}\right]Cl.$$

prepared from furfuraldehyde and 2-methylindole, forms spherical aggregates, m. p. 300° (decomp.), the base being obtained as a brown precipitate on addition of sodium hydroxide solution. When suspended in acetone and treated with diazomethane, the hydrochloride loses nearly all its chlorine.

From an ethereal solution of ferric chloride, diazomethane withdraws 6·71% of the chlorine. T. H. P.

Calorimetric Investigations on Melanins. FRANZ VON HOEFFT (*Biochem. Zeitsch.*, 1920, **104**, 1—8).—With the object of obtaining information indicative of the mechanism of formation of melanins, the author has determined the heats of combustion of various melanin preparations and of certain allied acids. The view that the formation of melanins in the integuments has its origin in tyrosine, or in the dihydroxyphenylalanine resulting from the oxidation of tyrosine, is not controverted by the author's results, the heat of combustion of tyrosine being of the same order of magnitude as that of the hippomelanin and that of one of the two liver melanins examined. On the other hand, the melanoidic acids formed during the hydrolysis of proteins by concentrated mineral acids are almost undoubtedly derived from tryptophan.

T. H. P.

Hippomelanin. III. OTTO RIESSER and PETER RONA (*Zeitsch. physiol. Chem.*, 1920, **109**, 16—31).—The authors have repeated and extended their earlier work (A., 1908, i, 1028; 1909, i, 749) on the decomposition of hippomelanin by the action of 3% hydrogen peroxide solution. The results obtained show that the criticisms of Adler-Herzmark (A., 1913, i, 500) are not justified, and that the experiments made by this author were inadequate.

Great difficulty is experienced in ridding the melanin of admixtures, but, after thorough purification, the preparations obtained always gave guanidine and ether-soluble acids in small yields when subjected to oxidising decomposition by means of hydrogen peroxide. That the proportion of guanidine separated represents only a minimal value is shown by the observation that guanidine carbonate is largely destroyed by hydrogen peroxide at steam-bath temperature. When the action of the hydrogen peroxide is sufficiently protracted, a large proportion of the carbon of the melanin undergoes oxidation to carbon dioxide. Gradual

oxidation of melanin by means of hydrogen peroxide in ammoniacal solution promises to yield more characteristic decomposition products. T. H. P.

Relation of the Free Amino-groups to the Lysine Content in Proteins. K. Felix (*Zeitsch. physiol. Chem.*, 1920, **110**, 217—229).—The author has estimated the nitrogen titratable with formalin in hydrolysed and unhydrolysed arachin (from *Arachis hypogaea*), glycinin (from *Soja hispida*), and gelatin, and draws the conclusion that the fraction of the hydrolysed protein which is precipitated by phosphotungstic acid after the removal of the other diamino-acids contains another nitrogenous substance besides lysine. The author further considers that Van Slyke's assertion (A., 1914, i, 212) that the free amino-groups of unhydrolysed proteins contain exactly one-half of the nitrogen of the lysine in the protein molecule is not justified. He suggests that the grouping of the amino-acids in the molecule may vary with the individual protein. S. S. Z.

Chemical Constitution of Adenine Nucleotide and of Yeast-nucleic Acid. W. Jones (*Amer. J. Physiol.*, 1920, **52**, 193—202).—When adenine nucleotide is hydrolysed by 5% sulphuric acid at 100°, the purine group is split off much more rapidly than the phosphoric acid; further, adenine nucleotide is a dibasic acid, indicating that only one hydrogen of the phosphoric acid has been replaced. These facts necessitate the union of phosphoric acid to carbohydrate, and that, in turn, to adenine. The structure of adenine nucleotide is thus similar to that of guanine nucleotide (A., 1917, i, 597). When yeast-nucleic acid is hydrolysed with mineral acid, the rate at which phosphoric acid is set free corresponds practically with the composite rate calculated for a mixture of the four nucleotides. If yeast-nucleic acid is a chemical combination of the four nucleotides, then in this union the phosphoric acid group of the nucleotides is not disturbed and the nucleotide linkings cannot be through phosphoric acid groups. Adenine and guanine are split off from their respective nucleotides and from yeast-nucleic acid by acid hydrolysis with equal rapidity. This shows that in yeast-nucleic acid the linkings cannot be through the purine groups, and probably not through the pyrimidine groups. By this process of elimination, the nucleotide linkings in yeast-nucleic acid must be through the only remaining group, namely, the carbohydrate. Chemical Abstracts.

Action of Boiled Pancreas Extract on Yeast-nucleic Acid. W. Jones (*Amer. J. Physiol.*, 1920, **52**, 203—207).—When an aqueous extract of pig pancreas is boiled and filtered, all its active agents but the one that decomposes yeast-nucleic acid into nucleotides, are destroyed. The extract will not act on thymus-nucleic acid. When yeast-nucleic acid is converted into nucleotides by this active agent, there is not the slightest change in acidity. This is regarded as the crucial test which proves that the nucleotide

inkings in yeast-nucleic acid are not through phosphoric acid groups. A structural formula for yeast-nucleic acid is suggested having the nucleotide linkings through the carbohydrate groups (compare preceding abstract). CHEMICAL ABSTRACTS.

Preparation of Adenine Nucleotide by Hydrolysis of Yeast-nucleic Acid with Ammonia. W. JONES and A. F. ABT (*Amer. J. Physiol.*, 1920, **50**, 574—578).—Adenine-uracil-dinucleotide as prepared by Jones and Germann (A., 1916, i, 515) appears to be a mixture of adenine nucleotide and uracil nucleotide. Using the method of Jones and Kennedy (A., 1919, i, 360), the authors separated from the mixture adenine nucleotide, which had the composition required by the formula $C_{10}H_{14}O_7N_5P,H_2O$. The mother liquor from the adenine nucleotide yielded the brucine salt of uracil nucleotide. CHEMICAL ABSTRACTS.

Carbohydrate Derivatives of the Mucoids and Mucins. O. SCHMIEDEBERG (*Arch. expt. Path. Pharm.*, 1920, **87**, 31—47). —The hyaloidin content of the mucoids and the mucins is calculated from the analytical results obtained by other investigators for some of these compounds. In the case of ovomucoid, the author also calculates the hyaloidin from the reduction figures obtained by hydrolysing the compound with hydrochloric acid. The communication contains a theoretical discussion of a series of compounds containing hyaloidin. S. S. Z.

Nitrogenous Carbohydrate Compounds of Protein. O. SCHMIEDEBERG (*Arch. expt. Path. Pharm.*, 1920, **87**, 1—30).—Nitrogenous products, termed by the author hyaloidin, were obtained as cleavage products from egg-white, ovarial fluid, mucin from pig's stomach, and fibrin. Egg-white was treated with 2—3% potassium hydroxide solution at the ordinary temperature until it dissolved, and then boiled for four to five hours with 10% alkali. After precipitating the protein with acetic acid, the concentrated filtrate was treated by the copper-potassium hydroxide method, and further traces of protein were precipitated with alcohol. The hyaloidin was then obtained from this fraction either by precipitation with lead acetate or by treatment with hydrogen peroxide, and contained copper and chlorine. *Hyaloidin* prepared from ovarial fluid has the composition $C_{26}H_{46}O_{20}N_2,\frac{1}{4}H_2O$. This hyaloidin and that obtained from *Echinococcus* have the same reducing capacity after boiling with hydrochloric acid. Hyaloidin obtained from egg-white had a similar composition and the same reducing power. Hyaloidin derived from mucin of pig's stomach also shows a reducing capacity of the same order. The author concludes that hyaloidins from the above sources are identical, and suggests that the molecule contains two glucosamine, two hexose, and one acetyl group. *Fibrin-hyaloidin* obtained from fibrin,

$$C_{30}H_{54}O_{24}N_2,$$

is different from those already discussed, and, in the author's

opinion, contains two glucosamine and three hexose groups, one of which is lævulose. The structure of the compound is discussed.

S. S. Z.

Theory of the Action of Diastase. GERTRUD WOKER (*Biochem. Zeitsch.*, 1919, **99**, 307—316).—A reply to Wohlgemuth's criticism (A., 1919, i, 361) of the author's theory of the action of diastase.

S. S. Z.

Formation of the Gum, Levan, by Mould Spores. I. Identification and Estimation. II. Mode of Formation and Influence of Reaction. NICHOLAS KOPELOFF, LILLIAN KOPELOFF, and C. J. WELCOME (*J. Biol. Chem.*, 1920, **43**, 171—187).—Mould spores (*Aspergillus sydowi*, Bainier) contain an enzyme capable of forming gum in sucrose solutions of all concentrations up to the saturation point. The gum is levan, m. p. about 200°; it yields lævulose on hydrolysis, and in the pure condition has $[\alpha] -40 \cdot 9°$. The invertase method may be applied to the estimation of sucrose in the presence of gum. The gum itself may be estimated polariscopically by using a combination of the Clerget and invertase methods.

Levan is formed by levanase from mould spores most readily from "nascent" dextrose and lævulose, but it appears that the latter is utilised to a greater extent than the dextrose. Only a slight formation of gum was obtained with reducing sugars in the absence of sucrose. The activity of levanase is influenced by the reaction of the medium. The optimum reaction occurs at about p_H 7·0.

J. C. D.

Preparation of Highly Active Saccharases. III. The Purification of F-preparations by Dialysis. H. VON EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1920, **110**, 175—190).—Several of the authors' saccharase F-preparations were submitted to fractional dialysis through a collodion membrane. It was found that the carbohydrate content of the enzyme increased as the dialysis proceeded until a point was reached at which it became stationary. The authors are therefore of opinion that saccharase must consist chiefly of carbohydrates. On the other hand, the nitrogen content of the dialysed saccharase diminished and reached a limit rather higher than that obtained previously (*Zeitsch. physiol. Chem.*, 1919, **109**, 65). These experiments show that saccharase does not require a co-enzyme for its function. S. S. Z.

Toxic Actions in Enzymic Processes. I. Inactivation of Saccharase by Heavy Metals. H. VON EULER and OLOF SVANBERG (*Fermentforsch.*, 1920, **3**, 330—393; from *Chem. Zentr.*, 1920, iii, 200—201).—The experiments were performed by observing the inversion of sucrose by the saccharase solution used previously (*Zeitsch. physiol. Chem.*, 1919, **107**, 273). It is found that the toxic power of the silver ion towards saccharase is considerably

greater than that of the mercuric ion. The enzyme is thereby inactivated, but not destroyed, since its power is completely restored by removal of the heavy metal or by converting it into an insoluble form (by hydrogen sulphide). The graph showing the relationship between toxicity and concentration in the case of mercuric chloride resembles the dissociation curve, whereas complete proportionality is found in the case of silver nitrate. The substrate (sucrose) exercises a considerable protective action towards metallic poisoning, which must be taken into account in calculating the necessary amount of poison per enzyme unit. With small amounts of mercuric chloride, the coefficient of inversion falls rapidly with the time. The degree of poisoning also depends on the length of time during which the mercuric chloride and saccharase are in contact previous to inversion; "self-regeneration" of the enzyme occurs gradually, the process appearing to be analogous to the "Danysz" effect in immunochemistry. The concentration of free silver ions becomes greatly diminished after addition of the enzyme solution to a dilute solution of silver nitrate, but metallic or colloidal silver is not formed, so that it would appear that union occurs with some components of the enzyme solution; it is found by electrometric measurement that each c.c. of enzyme solution (containing 56 mg. of dry substance) requires from 28 to 55 mg. of silver. The toxic action of auric chloride towards saccharase is of the same order as that of mercuric chloride, whilst copper sulphate is much less poisonous, and cadmium sulphate, thallium sulphate, and uranium nitrate are scarcely toxic.

The previous data concerning the inhibition of enzyme actions by heavy metals are collected. H. W.

Artificial Zymogens. MARTIN JACOBY (*Biochem. Zeitsch.*, 1920, **104**, 316—322).—The name artificial zymogen is given to enzymes inactivated by nickel or by mercuric chloride, this inactivation being assumed to be due to the formation of complex compounds of the enzyme with the inactivating substance.

Inactivation of urease is effected by means of minimal proportions of nickelous oxide, whereas a somewhat large quantity of the undissolved metal is required for the same purpose; it is now found that only the slight traces of metal passing into solution are active in this respect. In order to decide whether the nickel combines with the enzyme molecules or whether the metal in the free state in solution prevents the enzymic action, inactivated urease solution was subjected to dialysis, its action on carbamide being then examined both before and after activation by means of potassium cyanide. It is found that the zymogen is not activated by dialysis alone, but remains in the dialysed solution. The conclusion is drawn that the nickel forms an actual compound with the enzyme. Experiments made in presence of glycine indicate that the nickel enters the amino-acid compound, thus leaving the zymogen and escaping dialysis; in this way, the enzyme is rendered active.

T. H. P.

Preparation of *o*-**Guätholmonomethyltrioxyarsenomenthol.** LFRED MAUERSBERGER (D.R.-P. 320797; from *Chem. Zentr.*, 1920, ·, 293).—(i) Mentholguätholsulphuric ester is condensed with isodium monomethyl arsenate. (ii) Sodium benzenedisulphonate treated with sodium ethoxide, and subsequently with sodium ·senite; the intermediate product so obtained is treated with ethyl menthylsulphate. Mentholguätholsulphuric ester is a rown, oily liquid. The final product is a viscous mass, which ›lidifies at about 22° and has b. p. 154° (decomp.); it is expected › find application in pharmacy. H. W.

Synthesis of Boranilides. I. Boranilide and its Derivtives. TARINI CHARAN CHAUDHURI (T., 1920, **117**, 1081—1086).

Elements of the Oxygen Group and Organo-magnesium ompounds. M. GIUA and F. CHERCHI (*Gazzetta*, 1920, **50**, i, 52—377).—The action of tellurium on magnesium phenyl bromide similar to that of sulphur or selenium, and results in the formion of phenyl telluromercaptan, diphenyl ditelluride, phenyl ·lluride, and, in small proportion, hydrogen telluride: .) MgPhBr + Te = Ph·Te·MgBr, and the latter + HCl = MgClBr + ePhH; (2) 2MgPhBr + 2Te = $TePh_2$ + $Te(MgBr)_2$, and the latter · 2HCl = TeH_2 + 2MgClBr. The amount of hydrogen telluride idicated by equation (2) is, however, greater than that actually ·rmed when the complex is treated with dilute acid. The formion of phenyl telluride appears to be due to decomposition of ıe phenyl telluromercaptan, as this readily undergoes oxidation › diphenyl ditelluride, which decomposes into tellurium and phenyl ·lluride.

The action of sulphur, selenium, or tellurium on magnesium yrryl iodide yields black, infusible compounds which, from their roperties, are pyrrole-blacks containing, respectively, sulphur, ·lenium, and tellurium (compare Angeli and Pieroni, A., 1919, 134). These results indicate the complete chemical analogy cisting between tellurium and the other elements of Group VI the periodic system. The possible existence of isotopes in the ıse of tellurium is discussed.

Phenyl telluromercaptan, PhTeH, is unstable, but with mercuric ıloride forms the compound, TePh·HgCl (compare Lederer, A., 915, i, 1056), m. p. 85—90° (decomp.); it yields also a grey *auriıloride*, m. p. 154—156°, and a yellow, amorphous *platinichloride*, .. p. 75—80°.

The products obtained by the action of tellurium on magnesium ıenyl bromide were fractionated at a pressure of 85 mm. When ·eated with concentrated sulphuric and nitric acids, the fraction ıving b. p. 155—200° yields a pale yellow, amorphous substance [$(NO_2{\cdot}C_6H_4)_2TeO$], which contains 6·44% N and does not melt at 50°.

The residue failing to distil at 200° gives, when treated with ·ncentrated nitric acid, (1) phenyltelluric acid nitrate, $_6H_5O_4NTe$, m. p. 210—212° (Lederer, *loc. cit.*, gave m. p.

2—233°); the latter is decomposed by sodium hydroxide, giving e compound, $O(TePh_2{\cdot}NO_3)_2$, m. p. 223—224° (compare Lederer, c. cit.). (2) A compound which separates in minute, shining, hite crystals, m. p. 66—68°, and at a higher temperature becomes lid, and then has m. p. 201—203° (decomp.); this compound ses 2·89% at 80—90°, the formula $O{:}TePh{\cdot}NO_3,2EtOH$, corre- onding with 2·46% of alcohol, and $Te_2O_7N_2Ph_4,6EtOH$ with 82%.

The same fraction (above 200°) reacts energetically with bromine ethereal solution, giving the *compound*, $Te_2Br_4Ph_2$, which *forms* ining, yellow crystals, m. p. 200°, becoming opaque in the air, id loses part of its bromine when treated with alkali carbonate hydroxide.

Analysis of the black compound resulting from the action of lphur on magnesium pyrryl iodide gave: N 13·06—13·37, 21·67, and ash 0·205%. T. H. P.

Physiological Chemistry.

Relative Value of Fat and Carbohydrate as Sources of uscular Energy. With Appendices on the Correlation etween Standard Metabolism and the Respiratory Quotient uring Rest and Work. August Krogh and Johannes Lindhard ith Göran Liljestrand and Knud Gad Andersen] (*Biochem.* , 1920, **14**, 290—361).—An elaborate and valuable study of this nportant question. A method of determining the respiratory xchange of human subjects is described which admits of a high egree of accuracy. All the results agree in showing that work more economically performed on carbohydrate than on fat. A ypothesis regarding the physiological utilisation of fat and carbo- ydrate during work is advanced. J. C. D.

Habituation to Bromine Vapour and Action of the Latter n the Blood. S. Marino (*Arch. farm. sper. sci. aff.*, 1920, **29**, 3—64).—Respiration of bromine vapour causes diminution of the umber of red corpuscles and of the content of hæmoglobin in the ood. The extent of this diminution increases with the quantity the vapour administered, but not with repetition of the treat- ent. Habituation of the animal organism to bromine vapour is ttainable by gradual increase of the dose, but even continued nall doses produce hæmolysis. The vapour conditions marked icrease in the leucocytes, sometimes to about four times their ormal number. T. H. P.

Injurious Action of Carbon Dioxide on Red Blood orpuscles. W. Patzschke (*Zeitsch. physiol. Chem.*, 1920, **109**, —11).—Experiments in vitro show that carbon dioxide increases

by fifty or one hundred times the action of inorganic blood poisons which form methæmoglobin, the incidence of the reaction being accelerated markedly by rise of temperature. In presence of aniline or nitrobenzene, the formation of methæmoglobin in human blood occurs only after introduction of carbon dioxide. It is therefore probable that the development of the action of certain poisons in the veins is brought about by the carbon dioxide present. Intensification of the formation of methæmoglobin by carbon dioxide is produced, not only in suspensions, but also in solutions of blood corpuscles and in hæmoglobin solutions, so that it may be assumed that the carbon dioxide induces changes in the hæmoglobin favourable to the formation of methæmoglobin. Blood corpuscles charged with carbon dioxide are labile cells readily accessible to injury, whereas oxygen protects the corpuscles. T. H. P.

Antigens and Serological Specificity. XIV. Specific Serum Reactions with Simple Compounds of Known Constitution (Organic Acids). KARL LANDSTEINER (*Biochem. Zeitsch.*, 1920, **104**, 280—299. Compare this vol., i, 260).—The experiments now described show that with diazotised aniline-*m*-sulphonic acid, *p*-arsanilic acid, *o*-toluidine-5-sulphonic acid coupled with tyrosine, *m*-hydroxybenzoic acid, and salicylic acid the precipitin reactions of the corresponding azo-proteins are completely or almost completely destroyed; the action is a specific one, the specificity resembling that of the precipitin reactions of the azo-proteins themselves. Not only are the precipitations prevented by these azo-compounds, but with the help of the latter the precipitates, when formed, may, after centrifugation and washing, be dissolved. These inhibiting substances contain a group identical with the specific group of the corresponding azo-protein with which the immune serum employed reacts. The assumption may therefore be made that the inhibiting body combines with the anti-substance of the immune serum, and so prevents this from acting on and precipitating the azo-protein present in the solution. Such specific serum reactions with synthetic compounds of known constitution represent a new discovery.

Experiments have been made with simpler compounds in the same way as with the azo-colouring matters. As regards the azo-components corresponding with the immune sera, sodium *m*-aminobenzenesulphonate and *p*-aminophenylarsinate in neutral solution exhibit selective inhibiting action. In equimolecular proportions, the azo-colouring matters act considerably more strongly than the simple amino-acids, although these act at moderately low concentrations. The connexion between inhibiting effect and chemical constitution has further been investigated with a large number of other compounds, such as amino-acids and carboxylic, sulphonic, and arsinic acids free from amino-groups.

Of the various monobasic, polybasic, saturated, unsaturated, and substituted aliphatic carboxylic acids, most produce no, and none marked, inhibition of the precipitin reaction with the immune sera. With the aromatic and cyclic carboxylic acids, the action depends

on the constitution. The results obtained with benzene derivatives depend less on the character of the substituents than on their position, although the carboxyl group has a somewhat greater influence than other substituent groups. The results obtained are given in detail and discussed. T. H. P.

Formation of Protein from Carbamide by Ruminants. E. Salkowski (*Zeitsch. physiol. Chem.*, 1920, **109**, 276—279).—As regards the source of the sulphur of the protein formed in sheep fed with straw previously treated with sodium hydroxide (this vol., i, 699), it appears that the sheep were supplied with various inorganic salts, including potassium sulphate and sulphide. Estimation of the sulphur in the ash of straw treated with sodium hydroxide according to Beckmann's method shows that it is only just sufficient, if completely utilisable, to furnish the sulphur of the flesh formed by the sheep during the experiment; if the organically-bound sulphur of the straw is included, more than sufficient sulphur is supplied. The source of the tryptophan still remains an open question. T. H. P.

Taurine from Herring Flesh and its Crystallographic Investigation. E. Berner (*Zeitsch. physiol. Chem.*, 1920, **110**, 172—174).—The author has separated about 0·003% of taurine from the flesh of the herring (*Clupea harengus*), and has obtained it in exceptionally well-developed crystals belonging to the prismatic class of the monoclinic system: $a:b:c = 0·6817:1:0·9073$, $\beta = 93°47'$. T. H. P.

Formation of Oxalic Acid in the Animal Body. Ludwig Pincussohn (*Biochem. Zeitsch.*, 1919, **99**, 276—297).—Nucleic acid, xanthine, guanine, uric acid, and allantoin when introduced into the system of dogs and rabbits, either per os or by intravenous injection, produce an increase in the content of oxalic acid and a decrease in the allantoin content of the urine. The uric acid remains constant. Similar observations were made in a more pronounced way when the substances were previously "sensitised" and exposed to light. S. S. Z.

Amino-acid Synthesis in the Animal Organism. Can Norleucine Replace Lysine for the Nutritive Requirements of the White Rat? Howard B. Lewis and Lucie E. Root (*J. Biol. Chem.*, 1920, **43**, 79—87).—Eighteen per cent. of gliadin as the sole source of protein in the diet of a young rat will not permit growth until the inadequacy of lysine is made good. Neither *dl*-norleucine nor *d*-norleucine is able to supply the deficiency of a gliadin diet as does a supplement of lysine. J. C. D.

Relation of Urochrome to the Protein of the Diet. K. F. Pelkan (*J. Biol. Chem.*, 1920, **43**, 237—242).—The excretion of

rochrome appears to be dependent on the amount of protein in he diet.

A substance, protochrome, which gives similar reactions to rochrome, can be produced from certain proteins. All evidence oints to the fact that urochrome, lactochrome, and protochrome re identical, and, at least to a large extent, are derived from the ood proteins. J. C. D.

Presence of Iodine in Large Quantities of Sheep Pituitary lands. EMILY C. SEAMAN (*J. Biol. Chem.*, 1920, **43**, 1—2).—No dine was detected in quantities of sheep pituitary gland as large s 100 grams (compare Denis, A., 1911, ii, 746). J. C. D.

Decomposition Products of Atractylin in the Animal rganism. A. PITINI (*Arch. Farm. sper. Sci. aff.*, 1920, **29**, 8—96).—In an alkaline medium, atractylin, which has the robable formula $C_{30}H_{52}O_{18}S_2K_2$, decomposes, yielding sulphuric nd valeric acids, a carbohydrate, and a complex product (*A*), hich is obtained as a white powder, and gives the following actions: in concentrated sulphuric acid containing traces of formldehyde it dissolves to a red solution, which is turned deep blue y addition of a small quantity of water; with concentrated ılphuric acid and a few drops of aqueous vanillin solution, it ields an intense carmine-red coloration. By means of these actions, the gastro-intestinal contents and various organs of a og poisoned with atractylin were shown to contain this product *A*. T. H. P.

Relation of Hyaloidin to the Formation of Chondroitinılphuric Acid, Collagen, and Amyloid in the Organism. . SCHMIEDEBERG (*Arch. expt. Path. Pharm.*, 1920, **87**, 47—74). -A theoretical paper containing a critical discussion of the above ıbject. S. S. Z.

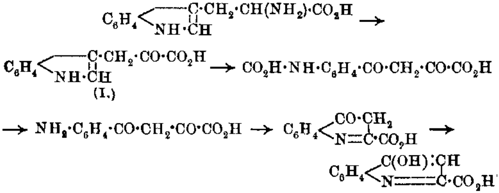
The Existence in the Bile of an Inhibitor for Hepatic sterase, and its Nature. GEORGE MACFEAT WISHART (*Biochem.* ., 1920, **14**, 406—417).—An inhibitory substance for the esterase f liver was found to be present in the bile of all the animals camined. It is probably the cholic acid portion of the bile acid olecules which is responsible for the effect. J. C. D.

Bioluminescence. I. The Luciferin and Luciferase of ypridina hilgendorfii. II. The Production of Light by ypridina hilgendorfii is not an Oxidation. S. KANDA (*Amer. Physiol.*, 1920, **50**, 244—260, 561—573).—I. Two substances, rresponding with luciferin and luciferase found by Dubois in *holas dactylus*, are concerned in the production of light by *ypridina hilgendorfii*. The first is thermostable; the second is estroyed by heat. Both are produced only in the maxillary gland lls of the animal. The author is of opinion that Harvey's theory ıd nomenclature (A., 1917, i, 365) are not tenable. II. The

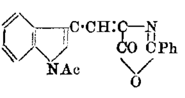
intensity of light produced by *Cypridina* in recently boiled water saturated with various gases was strongest in hydrogen and weakest in oxygen. Saturation with carbon monoxide, carbon dioxide, or nitrogen gave lights of intermediate intensities. It is concluded that the light cannot be produced by oxidation.

CHEMICAL ABSTRACTS.

Formation of Kynurenic Acid from Tryptophan in the Animal Body. A. ELLINGER and Z. MATSUOKA (*Zeitsch. physiol. Chem.*, 1920, **109**, 259—271. Compare A., 1914, i, 865).—The authors have synthesised indolepyruvic acid, and find that, when this acid is administered subcutaneously as sodium salt to a dog, it is possible to isolate from the urine kynurenic acid in amount rather less than one-half of that obtained when tryptophan is injected. The conclusion is drawn that the conversion of tryptophan into kynurenic acid is best represented by the scheme (compare Dakin, "Oxidations and Reductions in the Animal Body," 1912, 73; Barger and Ewins, A., 1917, i, 476):



The condensation of indole-3-aldehyde and hippuric acid in presence of acetic anhydride and sodium acetate yields, not the azlactone (compare Ellinger and Flamand, A., 1908, i, 378), but its 1-*acetyl* derivative (annexed formula), which crystallises in pale yellow rhombic or oblique rhombic plates, m. p. 205—206°, and, when treated with sodium hydroxide solution, yields



Indolepyruvic acid (formula I, above), which forms yellow ($+C_2H_4O_2$) or almost colourless crystals. Its p-*nitrophenylhydrazone*, $C_8H_6N\cdot CH_2\cdot C(CO_2H)\!:\!N\cdot NH\cdot C_6H_4\cdot NO_2$, crystallises in rosettes of yellow plates, m. p. 153—154°.

When quinoline-2-carboxylic acid is administered as sodium salt subcutaneously to a dog, it is separated in the urine partly unchanged and partly coupled with glycine, but does not undergo oxidation to kynurenic acid.

T. H. P.

Behaviour of Aspirin in the Animal Organism. A. PITINI (*Arch. Farm. sper. Sci. aff.*, 1920, **29**, 113—118).—Investigation

f the urine of dogs to which aspirin had been administered ndicates the presence of unchanged aspirin, so that part of the spirin is absorbed in the animal organism before undergoing ydrolysis. T. H. P.

Appearance of Acetaldehyde in the Body due to Cleavage f Ethyl Alcohol. WILHELM STEPP (*Arch. expt. Path. Pharm.*, 920, **87**, 148—153).—The presence of acetaldehyde was estabished in the blood and urine of a human subject who had previously onsumed ethyl alcohol. In the case of a dog which had received thyl alcohol, acetaldehyde was found in the urine, but not in the lood. S. S. Z.

Chemistry of the Proteins. The Species Specificity of he Structure of Protein. E. HERZFELD and R. KLINGER Biochem. Zeitsch., 1919, **99**, 204—219).—A theoretical paper in which the structure of protein molecules in relation to immunity nd heredity phenomena, and the mechanism of protein synthesis nd degradation, are discussed. S. S. Z.

Nature of Anaphylaxis. EMIL ABDERHALDEN and ARTHUR VEIL (*Zeitsch. physiol. Chem.*, 1920, **109**, 289—297. Compare A., 1912, ii, 1194).—The authors have treated guinea-pigs by subutaneous or intraperitoneal injection with glycine and its polyeptides up to heptaglycylglycine, but no phenomena were obtained esembling anaphylactic shock, with the exception of slight variaions in the temperature. From the heptapeptide onwards, the njection causes a characteristic skin affection.

Methods are described for preparing glycine ethyl ester hydrohloride in large amounts from chloroacetic acid, and pentaglycyllycine from tetraglycylglycine and chloroacetyl chloride.

T. H. P.

Chemical and Morphological Studies on Cholesterol and s Esters in Normal and Pathological Organs. JOHAN FEX Biochem. Zeitsch., 1920, **104**, 82—174).—The author's investigaons show that Windaus's digitonin method (A., 1910, ii, 462), as odified by Thaysen (A., 1914, ii, 498), is the only method yet escribed giving trustworthy results for the estimation of cholesterol i its pure solutions. Preliminary drying in a current of air of he organs from which the cholesterol and its esters are to be xtracted is not to be recommended, but treatment of the organs ith 2% sodium hydroxide solution and extraction of the alkaline olution with ether result in quantitative extraction and in an xtract of such purity that the cholesterol and its esters may be stimated exactly by the above method.

The proportions of free and combined cholesterol in the liver how very slight variations in all the cases examined, including wo of cirrhosis of the liver. In the kidneys, of both normal and iseased individuals, the free cholesterol varies but little in amount, nd the same holds for the combined cholesterol, even in the cases

of diabetes, pernicious anæmia, cirrhosis of the liver, and sepsis examined; with diseases of the kidneys, however, the normal small proportion of cholesterol present as ether is considerably exceeded. Inconsiderable variations occur in the proportion of free cholesterol in the suprarenal glands, but the combined cholesterol exhibits wide differences in different cases, the highest amounts being found in two instances of kidney disease and in one normal instance. In no case examined was cholesterol detectable morphologically in the liver, but with kidney disease of long standing the ester of cholesterol may be discovered morphologically in the kidneys in amount corresponding well with that found chemically.

T. H. P.

The Colloid Chemical Importance of Physiological Ionic Antagonism and of Equilibrated Salt Solutions. S. M. NEUSCHLOSZ (*Pflüger's Archiv*, 1920, **181**, 17—39; from *Chem. Zentr.*, 1920, iii, 312).—It has not been well established that the physiological action of ions depends solely on their relationship to the proteins, and that these relationships are purely chemical in character. In many physiological phenomena, in the cell, lipoids play a predominating rôle. Solutions of lecithin (2%) have been treated with equal quantities of salt solutions and their surface tensions determined stalagmometrically. The chlorides of the cations Na, K, Ca, Mg, and Al noticeably increase the surface tension of lecithin solutions. With mixtures of these salts, an antagonism between the cations is very obvious. The surface tension of a lecithin solution in the presence of a mixture of salts is dependent, in the first place, on the relative ratio of concentration of the cations, and is not influenced within wide limits by the absolute concentration of the solution. A far-reaching parallelism exists between physiological and colloidal chemical ionic antagonism as shown in this manner. The physico-chemical basis of ionic antagonism is found in the capacity shown by the cations of mutual replacement from their adsorption compounds (in this case from the surface of the lecithin particles), but the displacing ion does not take the place of that displaced.

H. W.

Water-soluble Vitamines. I. Are the Antineuritic and the Growth-promoting Water-soluble-*B* Vitamines the Same? A. D. EMMETT and G. O. LUROS (*J. Biol. Chem.*, 1920, **43**, 265—286).—Experiments designed to ascertain whether these two substances are identical lead the authors to suggest, tentatively, at least, that they are not the same. The antineuritic factor appears to be more readily decomposed by heat. The lack of strictly quantitative methods renders the conclusion indefinite.

J. C. D.

Toxic Action of Cyanogen Chloride. C. I. REED (*J. Pharm. Expt. Ther.*, 1920, **15**, 301—304).—This action is primarily due

to the formation of hydrocyanic acid, but in delayed poisoning the chlorine may also have an effect. Protection may be given by sodium thiosulphate. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Control of the Purity of Preparations of Carbohydrate by Bacterial Fermentation Tests. H. O. Schmit-Jensen (*Compt. rend. Soc. Biol.*, 1920, **83**, 699—701; from *Chem. Zentr.*, 1920, iv, 217).—Different types of bacteria can be investigated by their action towards different carbohydrates (*Compt. rend. Soc. Biol.*, 1920, **83**, 502); conversely, the purity of carbohydrates and polyhydric alcohols can be tested by fermentative action if the necessary classes of bacteria are available. H. W.

Proteins of Putrefactive Bacteria. E. Salkowski (*Zeitsch. physiol. Chem.*, 1920, **109**, 49—56).—Putrefactive bacteria are found to contain two protein compounds, one having the characters of the albumoses and the other those of a globulin-like protein. Neither contains the tryptophan group, whilst the atomic complex giving the xanthoprotein reaction is almost entirely lacking with the albumose and present in extremely small proportion in the protein. When heated in a narrow test-tube, both emit vapour capable of blackening lead acetate paper (Siegfried's reaction), whereas this behaviour is not shown by the proteins and is doubtful with the albumoses.

Since Siegfried's reaction was unknown to Nencki, it is possible that the latter's anthraxprotein (A., 1885, 178) is not quite free from sulphur. Further work is necessary to ascertain if unicellular organisms are able to produce proteins not lacking in cyclic and beterocyclic groups, but possibly this power is restricted to the true plants, among which bacteria and yeasts cannot be placed. Between plants and animals lies a third group of organisms, which are able to ntilise inorganic nitrogen to build up their body-substance, but are unable, apparently owing to absence of chlorophyll, to convert inorganic into organic carbon.

Voeltz (*Berlin Klin. Woch.*, 1919, No. 29) fed sheep for seventeen to twenty-five days solely on straw (treated with sodium hydroxide and free from digestible nitrogen), sugar, starch, and carbamide, growth and accumulation of protein taking place. The sources of the sulphur and the tryptophan group of the protein formed are obscure. T. H. P.

The Enzymes of B. Coli communis which are Concerned in the Decomposition of Dextrose and Mannitol. IV. The Fermentation of Dextrose in the Presence of Formic Acid. Egerton Charles Grey (*Proc. Roy. Soc.*, 1920, [*B*], **91**, 294—305). —The products obtained in the decomposition of dextrose by

Bacillus coli communis are divided into three groups: (1) lactic acid; (2) acetic acid, alcohol, and succinic acid; (3) formic acid, carbon dioxide, and hydrogen, there being a closer relationship between the products of groups (2) and (3) than exists between either group and group (1). The proportions in which the products of group (2) appear depend on the intimacy with which the reactions of this group co-operate with the reactions of group (3), and this further explains the fact that in many normal fermentations there is a tendency for groups (2) and (3) to appear as constituting one group.

It is now demonstrated that hydrogen, nascent during the fermentation, does take part in the production of alcohol, the hydrogen arising either from the decomposition of the dextrose itself or from the simultaneous fermentation of added calcium formate. It is also shown that the presence of calcium formate does not depress the formation of formic acid, and the consequent yield of its gaseous products, carbon dioxide and hydrogen, in the fermentation of dextrose by *B. coli communis*. W. G.

Action of Bacillus fluorescens liquefaciens (Flügge) on Asparagine in a Definite Chemical Medium. II. Products from, and Mode of Attack on, Asparagine. A. BLANCHETIÈRE (*Ann. Inst. Pasteur*, 1920, **34**, 392—411).—The chief products formed are acetic, malic, succinic, fumaric, and carbonic acids. The mechanism of their formation is discussed. J. C. D.

Influence of the Nature of the Carbonaceous Food on the Utilisation of Nitrogen by Bacillus subtilis. E. AUBEL (*Compt. rend.*, 1920, **171**, 478—480).—Glycerol gives a better yield of culture and a better utilisation of nitrogen than lævulose, and this in turn than dextrose, when added to the culture solution of *Bacillus subtilis*. The high yield of organism and increased utilisation of nitrogen with glycerol are probably due to its preliminary conversion into pyruvic acid, and it is noted that sodium pyruvate gives even better results than glycerol. W. G.

Experiments on Osmosis and on Aspiration due to Evaporation, Suitable for Use in Plant Physiology. PIERRE LESAGE (*Compt. rend.*, 1920, **171**, 358—360).—Simple modifications of the experiments of Dutrochet and Askenasy are described. W. G.

Fluorescence and Condition of Chlorophyll in Living Cells. KURT STERN (*Ber. Deut. bot. Ges.*, 1920, **38**, 28—35).—The author's spectroscopic investigations show that chlorophyll fluoresces only in true solution, colloidal chlorophyll solutions and solid chlorophyll exhibitiug no appreciable fluorescence. Observation of the fluorescence of turbid media with the naked eye leads to erroneous conclusions, spectroscopic examination being necessary to ascertain the real strength of the fluorescence. In the intact cell, the chlorophyll is contained in lipoidal, true, and fluorescing

solution. The process of assimilation proceeds partly in the lipoidal and partly in the hydroid phase, and surface-active substances alter the limiting surface between the two phases and thereby retard or assist assimilation. T. H. P.

Behaviour of certain Organic Compounds in Plants. XII. G. CIAMICIAN and C. RAVENNA (*Gazzetta*, 1920, **50**, ii, 13—46).—An account of work already published (A., 1919, i, 58, 140, 241; this vol., i, 408). T. H. P.

Enzyme Formation with Aspergillus niger. H. VON EULER and S. ASARNOJ (*Fermentforsch.*, 1920, **3**, 318—329; from *Chem. Zentr.*, 1920, iii, 201—202).—The investigation proceeded along lines similar to those adopted by Euler and Svanberg (A., 1919, i, 201, 614) in the case of saccharase in bottom yeast. As far as saccharase is concerned, it is found that the total enzyme action remains almost unchanged if the well-ground fungus material is brought into contact with sucrose solution either after being warmed to a temperature at which the saccharase is not damaged or after being dried with or without toluene. Wohlgemuth's method can only be applied with difficulty to the estimation of amylase by the direct action of the fungus material on starch solution; the sugar which is formed is best estimated by Bertrand's reduction method. For the type investigated, and under certain conditions, the inverting capacity, $I_f = k \times g$ sugar/g dry substance, is found to be $0{\cdot}32 \times 10^{-2}$. A fungus which had been grown on starch solution with the addition of peptone had a saccharase activity about 30% higher than that of a specimen grown under similar conditions but in the absence of peptone. Addition of peptone to the nutrient solution, which otherwise contains only inorganic nitrogen, also influences the formation of amylase. The data of other workers with regard to the improvement in the formation of amylase, due to addition of starch to the nutrient solution, could be quantitatively confirmed. H. W.

Water-soluble Vitamines. II. The Relation of the Antineuritic and Water-soluble Vitamines to the Yeast Growth-promoting Stimulus. A. D. EMMETT and MABEL STOCKHOLM (*J. Biol. Chem.*, 1920, **43**, 287—294).—Further evidence is given in support of the theory that the antineuritic and the growth-promoting vitamines are not identical. It is also possible that the substance which promotes cell-division in yeast is another factor of the vitamine type. It is therefore considered inadvisable to employ the quantitative method introduced by Williams (A., 1919, i, 463) until the differentiation of these factors has been satisfactorily accomplished. J. C. D.

Comparative Studies on Respiration. XI. Effect of Hydrogen-ion Concentration on the Respiration of Penicillium chrysogenum. F. G. GUSTAFSON (*J. gen. Physiol.*, 1920, **2**, 617—626).—Variations in the P_H value between 4 and 8

produce practically no effect on the normal rate of respiration of *Penicillium chrysogenum* (the rate at neutrality is considered normal). Increasing the P_H value to 8·80 causes respiration to fall to 60% of the normal, after which it remains stationary for the duration of the experiment. Decreasing the P_H value to 2·65 causes a gradual rise and a gradual return to the normal; at P_H 1·10 to 1·95 the preliminary rise amounts to 20%, and is followed by a fall to below the normal. The decreases in respiration brought about by solutions of a P_H value of 1·95 or less are irreversible, whilst a similar decrease which occurs at P_H 8·80 is reversible, the rate coming back to practically normal after the material is replaced in a neutral solution.

Determinations by means of Winkler's method showed an increase in the consumption of oxygen in acid solutions and a decrease in alkaline solutions. H. W.

Crystallisable Sugar and Free Acids in Plants. H. COLIN (*Compt. rend.*, 1920, **171**, 316—318).—The fact that sucrose exists in a large number of fruits in the presence of free acid at a concentration more than sufficient to cause its inversion is shown to be due to the presence of alkali salts of the organic acids in the juices, which lessen the hydrolysing action of the free acids. W. G.

Relation between the Calcium and the Nitrogen Content of Plants and the Function of Calcium. F. W. PARKER and E. TRUOG (*Soil Sci.*, 1920, **10**, 49—56).—From the consideration of a large number of analyses of various plants with respect to their nitrogen, phosphorus, potassium, calcium and magnesium content, it was observed that the only element the amount of which was closely related to the nitrogen content was calcium. These plants could be grouped in two classes, according to their calcium–nitrogen ratio. In one group the ratio was low, averaging 0·306, and this group consisted of plants of the grass family, which have a low lime requirement. In the other group the ratio was high, 0·553, and the group contained the legumes and other plants which have a high lime requirement and are sensitive to soil acidity. These results point to the conclusion that plants which have a high nitrogen or protein content, and therefore produce a large amount of acidity from protein metabolism, require a large amount of calcium as carbonate for the neutralisation of the plant acids. J. H. J.

Inulin in the Globe Artichoke. RUTH OKEY and ANNA W. WILLIAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 1693—1696).—In a sample of globe artichoke which, by the ordinary methods of analysis of foodstuffs, gave 6·8% of nitrogen-free extractives, the authors found 2·5% of inulin and altogether 4·2% of total carbohydrate extracted by water and 1% hydrochloric acid. W. G.

Enzyme Action in Echinodontium tinctorium, Ellis and Everhart. HENRY SCHMITZ (*J. gen. Physiol.*, 1920, **2**, 613—616).—The present paper is the second of a series dealing with the

physiology of wood-destroying fungi (compare Schmitz and Zeller, *Ann. Missouri Bot. Garden*, 1919, **6**, 193). In *Echinodontium tinctorium*, the presence of the following enzymes has been demonstrated: esterase, maltase, lactase, sucrase, raffinase, diastase, inulase, cellulase, hemicellulase, urease, rennet, and catalase.

H. W.

Carbohydrates of Lichen islandicus. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1920, **110**, 158—166. Compare A., 1919, i, 242). —The author confirms the statement of Errera (Diss., 1882) and others to the effect that *Lichen islandicus* contains two carbohydrates: (1) lichenin, which gelatinises when the hot solution is cooled and gives no reaction with iodine, and (2) a soluble carbohydrate which, contrary to the statment of Ulander and Tollens (A., 1906, ii, 193), gives a decided blue coloration when carefully treated with iodine solution; this coloration is, however, distinctly less intense than that obtained with starch, and it is possible that this carbohydrate, known as *iso*lichenin, is not a single individual, and that the iodine reaction depends on the presence of a third carbohydrate in small proportion.

The physical constitution of lichenin in the moist state suggests that this compound either belongs to the pectins or contains these. Dry lichenin does not, however, respond to the method for detecting pectin given by von Fellenberg (A., 1916, ii, 351), according to whom the pectins yield methyl alcohol when treated with sodium hydroxide solution.

T. H. P.

Kinetics of the Action of Catalase Extract from Marine Algæ, with a Note on Oxydase. HAROLD CLARK HAMPTON and LOURENS G. M. BAAS-BECKING (*J. Gen. Physiol.*, 1920, **2**, 635—649).—Preliminary investigations of the catalase, peroxydase, and oxydase of marine algæ are described, the present communication dealing only with *Ulva taeniata*, Setchell and Gardner. This contains a catalase, which adheres to the cells to a certain extent, but may, mechanically or by exosmosis, pass into the surrounding medium. This catalase is able to act on peroxide in a neutral medium, the reaction being unimolecular. In an alkaline medium, the catalase decomposes peroxide, following the formula of Schmidt-Nielsen, $K = \sqrt{a} - \sqrt{a-x}/t\sqrt{a(a-x)}$. The reaction time varies in a linear relation with the concentration of the peroxide. Reaction velocity and enzyme concentration vary in a linear relation. Reaction velocity and peroxide concentration vary in a continuous non-linear and non-exponential relation. Since the peroxide is in excess of the feeble catalase, these facts are in agreement with the data of Senter on blood catalase. On dilution, the enzyme is destroyed, following highly exponential lines, $dx/dt = K(a-x)^3$, or even $dx/dt = K(a-x)^4$.

Ulva taeniata contains oxydase; the presence of peroxydase is not proved.

H. W.

Extractive Substances of Melolontha vulgaris. DANKWART ACKERMANN (*Zeitsch. Biol.*, 1920, **71**, 193—202).—This organism is found to contain uric acid, leucine, putrescine, lysine, *p*-hydroxyphenylethylamine, choline, and either cholesterol or an allied sterol. Melolonthine (compare Schreiner, A., 1871, **24**, 1201), creatine, creatinine, betaine, and tyrosine could not be detected.

T. H. P.

Action of Rain Water on the Deposits from Copper Spray Liquids. G. VILLEDIEU and (MME) VILLEDIEU (*Compt. rend.*, 1920, **171**, 360—363).—Ordinary country rain water does not dissolve even traces of copper from the precipitate obtained in either *Bordeaux* or *Burgundy mixtures*. W. G.

Acidity of Japanese Acid Clay. KIUHEI KOBAYASHI (*J. Chem. Ind. Japan*, 1920, **23**, 543—549).—Japanese acid clay (Japanese fuller's earth) is a closely related mixture of colloidal hydrous aluminium silicates, $Al_2O_3,2SiO_2,xH_2O$, and an amorphous anhydrous compound of orthosilicic acid, SiO_2,xH_2O, and may be expressed by the formula $Al_2O_3,6SiO_2,xH_2O$, where x is more than 6. The clay itself is not a true acid substance, and the acidity is to be ascribed to its adsorptive property. Adding an acid clay to some basic dye solution, RCl, it may be supposed that the so-called Helmhorz double layer is formed on the surface of the clay, and that it adsorbs hydroxyl ions in accordance with its properties as an acid gel, whilst hydrogen ions are liberated. The radicle R combines with the hydroxyl ions and the hydrogen ions unite with chlorine ions of the basic dye; hydrochloric acid will therefore be liberated. Reaction between an acid clay and neutral potassium chloride solution similarly produces hydrochloric acid, which dissolves aluminium in the clay. The aluminium chloride thus formed will be decomposed by hydrolysis into aluminium hydroxide and hydrochloric acid. K. K.

The Occurrence and Nature of the Plant Growth-promoting Substances in various Organic Manurial Composts. FLORENCE ANNIE MOCKERIDGE (*Biochem. J.*, 1920, **14**, 432—450).—The ordinary organic manures used in horticultural and agricultural operations, namely, leaf-mould and fresh and well-rotted stable manure, and well-manured fertile soil, contain, in varying proportions, water-soluble substances, which are effective as plant growth-promoting substances, as is shown by the effect of their aqueous extracts on the development of plants of *Lemna major*. In all cases, the extract of rotted manure was more effective than that of the fresh material. All these materials contain appreciable quantities of nucleic acid and its derivatives in various stages of decomposition, and the greater the bacterial decomposition of the material concerned, the greater is the resolution of the original nucleic acid into its free bases. W. G.

Organic Chemistry.

Oxidation of Hydrocarbons by Oxygen. Oxidation of araffin. C. Kelber (*Ber.*, 1920, **53**, [*B*], 1567—1577. Compare ischer and Schneider, this vol., i, 519; Grün, this vol., i, 520).—ı a previous communication (this vol., i, 280), the author has ealt with the volatile acids obtained by the oxidation of paraffin; e now describes the investigation of the residual mass, which nounts to 90—100% of the initial material, and has iodine umber 1—2, saponification number 250—300, and acid number bout 200. The highly complex mixture of acids cannot be parated into its components by the ordinary methods, and only y a suitable combined process is it possible to isolate and identify rtain acids. At present, efforts have been mainly directed wards the characterisation of solid, saturated, normal fatty acids om $C_{10}H_{20}O_2$ onwards, such as occur in the animal and vegetable ganisms.

The crude residue is washed with water and then hydrolysed ith alkali hydroxide; after removal of unsaponifiable matter, the ids are liberated, and a fraction soluble in light petroleum is epared. This fraction is esterified with ethyl alcohol, and a ırtial separation is effected by distillation of the ethyl esters ıder diminished pressure. The ester fractions are separately drolysed, and the resulting acids are separated by suitable comnations of the following methods: (i) crystallisation of the acids, .) separation of the potassium salts by acetone (compare Fuchini ıd Dorta, A., 1914, ii, 153), (iii) the magnesium acetate method, ıd (iv) crystallisation of a mixture containing a suspected acid om *a saturated solution of that acid*. The *presence of the follow*g acids has so far been established: decoic, myristic, palmitic, ptadecoic, stearic, and arachidic, and an acid, $C_{16}H_{32}O_2$, which isomeric with palmitic and possibly identical with Bergmann's palmitic acid (A., 1918, i, 285). H. W.

The Chlorination of Ethylene in the Presence of Calcium lloride. [illegible] (*Gas J.*, 1920, **149**, 691—693).—A nple apparatus is described for use with Newth's method (T., 01, **79**, 915) for the preparation of ethylene, by means of which steady supply of the pure gas may be obtained. When the gas epared in this way is passed, along with chlorine, over a short yer of calcium chloride in a water-cooled tube, a mixture of chloroethane (50%), trichloroethane (25%), and less volatile comunds (25%) is obtained, and from this pure dichloroethane may adily be separated by fractionation. The trichloroethane probly results from the secondary action of chlorine on the dichloroıane, and not from the preliminary formation of vinyl chloride th subsequent addition of chlorine. The less volatile compounds e probably chloro-derivatives of polymerides of ethylene.

Dichloroethane behaves towards potassium carbonate in a p cisely similar manner to dibromoethane, giving ethylene glycol a vinyl chloride, but the action is much slower than with dibromoethane. W. G

The Interaction of Ethylene and Sulphuryl Chlori WILLIAM FOSTER (*Science*, 1920, **51**, 641—642).—At the ordin temperature, no apparent change occurs when ethylene is bubb through sulphuryl chloride. Under certain conditions, not m tioned, on continued passage of the gas the solution beco greenish-yellow, and the temperature rises to a maximum 35—40°. Then the solution becomes colourless, the temperat falls, and the colour reappears. This cycle is repeated often, ea time becoming longer and the temperature differences less p nounced. Some products of the reaction are ethylene dichlor and sulphur dioxide. The subject is still under investigation. CHEMICAL ABSTRACTS

Preparation and Characterisation of Ethylenebron hydrin. JOHN READ and REXFORD GEORGE HOOK (T., 1920, **1** 1214—1226).

Preparation of *iso*Amyl Alcohol by Pasteur's Meth FÉLIX MARTIN (*J. Pharm. Chim.*, 1920, [vii], **22**, 220—226).— the preparation of the amylsulphuric acids, which is the first st in the isolation of pure *iso*amyl alcohol from fusel oil by t fractional crystallisation of the barium amylsulphates, the b results are obtained with 90—91% sulphuric acid (D 1·820—1·82 using an excess of 15—20% above the theoretical quantity. Unc these conditions, about 60% of the alcohol is esterified, but as small proportion is apparently converted into the normal sulpha the actual yield of the acid sulphates amounts to about 50—55 If a large excess of sulphuric acid is used, considerable difficult are encountered later in the separation of the barium sulph without any adequate compensation in the increased percentage alcohol esterified. G. F. M

[Reactions and Derivatives of ββ'-Dichlorodietl Sulphide.] O. B. HELFRICH (*J. Amer. Chem. Soc.*, 1920, 4 1839).—The author states that certain of the physical consta (this vol., i, 525) previously given are incorrect. The followi are the corrected values: Line 24,* read "b. p. 222—223°/21 mm Line 20,* "m. p. 171°." Line 17,* "b. p. 173—175°/21 mm Line 13,* "b. p. 193—195°/22 mm." W. G.

Catalytic Reduction of Organic Compounds with t Aid of Nickel Carbonyl. RUDOLF LESSING (D.R.-P. 3219 from *Chem. Zentr.*, 1920, iv, 367).—(1) The catalyst is broug into action at the moment of decomposition of the nickel carbon (2) The nickel carbonyl and hydrogen or gases, which are ric in hydrogen than technical water-gas, are brought into cont with the substance to be hydrogenated at a suitable temperat

* From bottom.

during the whole course of hydrogenation. (3) The nickel carbonyl is dissolved in the substance under treatment, and the solution is injected into a heated vessel, in which it comes into contact with hydrogen or the hydrogenating agent.

Hydrogen containing 5—10% of carbon monoxide is used in the treatment of oils or fatty acids. The more volatile tar oils, benzene, etc., are heated to the requisite temperature with hydrogen containing nickel carbonyl; the preparation of aniline from nitrobenzene is effected similarly. H. W.

Keto-enolic Desmotropy. XII. The Fractional Distillation of Ethyl Acetoacetate. KURT H. MEYER and VIKTOR SCHOELLER (*Ber.*, 1920, **53**, [*B*], 1410—1416).—Ethyl acetoacetate has been distilled from a Jena-glass apparatus which had been cleaned by being steamed, washed with alcoholic hydrogen chloride, and dried at 100°. The operation was performed under 2 mm. pressure, and the ester was thus divided into four equal fractions and a residue in the flask; the former contained 78%, 76%, 72%, and 63%, respectively, of the enolic form, of which only 5% was present in the residue. The whole distillate is highly enolised, whilst an ester richer in the ketonic form remains in the flask. Special experiments show that enolisation only occurs to a slight extent in the vaporous phase, even when this is superheated and in contact with glass. The change seems to be mainly located on the walls of the neck of the flask and the column, where the condensed ketone, in boiling, is isomerised to the equilibrium ester, which evolves the more volatile enolic form. Since the desmotropic change was probably due to the catalytic action of the glass, the experiment was repeated, using a quartz flask with glass condenser and receivers; the enolic contents of three fractions and a residue, all of equal volume, were 22, 11, 2·5, and 0% respectively. The mean percentage of enol in distillates and residue combined was 8·9%, so that the ester was practically unaffected by the distillation. It appears beyond doubt that fractionation under "aseptic" conditions affords the readiest means of isolating the pure ketone, and the enolic form may also be isolated by repeated distillation of larger amounts. (The enolic content of the various fractions is deduced from their refractive indices, a graph showing the relationship between the two functions being given in the original.)

Methyl benzoylacetate has been similarly distilled from a glass flask; three successive fractions contained 40, 21, and 20% of the enolic form, which was present to the extent of 8% in the residue and 18% in the original ester. In this experiment, it is noteworthy that the first drops of the distillate solidified in the condenser, a sign of the presence of the almost pure enolic form. H. W.

Decomposition of the Acid Salts of Dibasic Acids in Aqueous Solution. V. TH. SABALITSCHKA (*Ber.*, 1920, **53**, [*B*], 1383—1387. Compare A., 1919, i, 433, and previous abstracts). —Aqueous solutions of the potassium hydrogen salts of malonic,

succinic, maleic, and fumaric acids have been extracted with ether, and the amount of acid removed has been determined; the partition-coefficient of the free acids between ether and water has been measured under identical conditions. The ethereal solution was found to contain about one-thirteenth of the malonic acid originally present in the acid salt, whilst the corresponding fractions for succinic and fumaric acids are one-sixth and one-fifth; further, the presence of free acid in the aqueous solution of the hydrogen maleate could not be detected. Protracted continuous extraction of an aqueous solution of potassium hydrogen succinate by ether showed that it is possible to remove nearly the whole of the acid portion by this means, but the process becomes very slow towards the end, partly by reason of the diminished concentration of the free acid in the aqueous solution, but also in consequence of the presence of relatively large quantities of normal salt. H. W.

The Electrosynthetic Preparation of *n*-Tetradecane-αω-dicarboxylic Acid. KARL STOSIUS and KARL WIESLER (*Biochem. Zeitsch.*, 1920, **108**, 75—81).—On electrolysing the potassium ethyl ester of azelaic acid, ethyl *n*-tetradecane-αω-dicarboxylate was obtained: $2CO_2Et{\cdot}[CH_2]_7{\cdot}CO_2K = CO_2Et{\cdot}[CH_2]_{14}{\cdot}CO_2Et + 2CO_2 + 2K$. From this the acid was obtained, and found, as expected, to be identical with thapsic acid, isolated by Canzoneri from juniper berries (A., 1884, 461). S. S. Z.

The Growth of Crystals of Potassium Sodium Tartrate. MISHIO ISHIMOTO (*Proc. Phys.-Math. Soc. Japan*, 1920, [3], **2**, 81). —The crystals of potassium sodium tartrate were obtained from the solution by very slow cooling. Successful growth depends on the rate of cooling and the evaporation of the liquid. The solution was kept in a 25-litre thermostat heated electrically. The vessel containing the solution was sealed practically air-tight to retard the evaporation of the liquid. The solution was prepared to be saturated at a temperature between 30° and 32°, and its rate of cooling was slow, about 0·2—0·4° per day. In such a way, crystals of 6—7 cm. in length were obtained in two weeks or more.
CHEMICAL ABSTRACTS.

Production of Saccharic Acid and Tartaric Acid from Carbohydrates. DIAMALT AKT.-GES. (Brit. Pat. 108494).—Saccharic and tartaric acids are readily obtained by oxidising carbohydrates with sulphuric and nitric acids, or sulphuric acid and oxides of nitrogen, peroxidised by treatment with air, ozone, or oxygen, at a temperature of 100°, in presence of oxidising catalysts, particularly molybdenum, mercury, or platinum. For example, 100 parts of starch are mixed with 150 parts of water and 3 parts of sulphuric acid and saccharified. Concentrated sulphuric acid (25 parts), nitric acid (D 1·4; 60 parts), and an oxide of molybdenum (1 part) are then added, and the reaction mixture is maintained at 100°, a further 100—140 parts of nitric

acid being gradually introduced. At the end of the operation, the nitric acid is evaporated, and, after diluting the residual liquor with water, the molybdenum is precipitated by hydrogen sulphide and the sulphuric acid and traces of oxalic acid by lime or baryta, and saccharic acid separated from the filtrate, after concentration, as potassium hydrogen saccharate. The yield amounts to 65%. If mercury is used as catalyst, and twice the quantity of nitric acid is added, a yield of 60% of potassium hydrogen tartrate, together with about 10% of saccharate, is obtained. G. F. M.

Mixed Dismutation of Aldehydes. F. F. Nord (*Biochem. Zeitsch.*, 1920, **106**, 275—280).—The reaction between two different aldehydes, expressed by the equations $R\cdot CHO + R_1\cdot CHO + H_2O = R\cdot CH_2\cdot OH + R_1\cdot CO_2H$ or $R_1\cdot CH_2\cdot OH + R\cdot CO_2H$, is termed mixed dismutation of aldehydes. According to Neuberg's theory of fermentation (Neuberg and Kerb, A., 1914, i, 118), such a reaction may be assumed to take place between the two intermediate products, methylglyoxal and acetaldehyde, in such a way that pyruvic acid and ethyl alcohol are formed until all the sugar is exhausted:

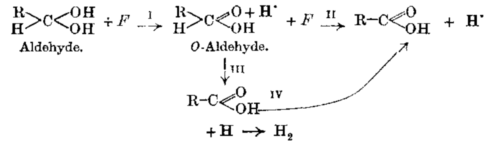
$$\begin{matrix} CH_3\cdot CO\cdot CHO \\ CH_3\cdot CHO \end{matrix} + \begin{matrix} O \\ | \\ H_2 \end{matrix} = \begin{matrix} CH_3\cdot CO\cdot CO_2H \\ CH_3\cdot CH_2\cdot OH \end{matrix}.$$

The author has investigated the reactions between the following pairs of aldehydes in presence of aluminium ethoxide as condensing agent: (1) acetaldehyde and *iso*valeraldehyde, (2) *iso*valeraldehyde and benzaldehyde, and (3) acetaldehyde and benzaldehyde. In each case, mixed dismutation occurs, the products in case (1), for instance, being ethyl acetate, amyl valerate, amyl acetate, and ethyl valerate. T. H. P.

The Dehydroxidation of Aldehydes. Mechanism of Oxidation. Erich Müller (*Annalen*, 1920, **420**, 241—261. Compare Müller and Hochstetter, A., 1914, ii, 615; Fichter, A., 1918, ii, 439).—It has been shown that when an alkaline solution of formaldehyde is electrolysed with a copper anode, equal volumes of hydrogen are initially evolved from either pole, but the evolution from the anode gradually ceases as the electrolysis proceeds; it is now found that the process occurs for an indefinite period when the anode is made of copper foil which has been covered with molten cuprous chloride and subsequently cathodically reduced in sodium hydroxide solution, or of silver foil which has been treated in a similar manner. A similar action takes place in the presence of certain metallic oxides, of which cuprous and cupric oxides, as well as silver oxide, have been particularly investigated; in these cases there is a period of incubation. The reaction has been extended to acetaldehyde and benzaldehyde, which are also found to be converted into the corresponding acid and gaseous hydrogen. The latter is also evolved in small quantity from alkaline solutions of formaldehyde in the presence of certain metals and in the

absence of particular oxidising agents; these metals also catalytic ally accelerate the Cannizzaro reaction.

The mechanism of oxidation is represented by the followin scheme:



in which F is the charge induced by the electric current or by a oxidising agent. The primary product of the oxidation of a aldehyde is the corresponding *O*-aldehyde; dehydroxidation occur if this is more readily oxidised according to III than in accordanc with II. Conversion of aldehyde into acid without evolution o hydrogen may occur along the lines I and II, or I, III, and IV Whether or not hydrogen is evolved during the oxidation of th aldehyde in the presence of catalysts depends on whether the latte accelerate III more than IV. H. W.

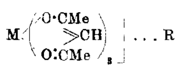
Quantitative Investigation of Cannizzaro's Reaction i the Condensation of Acetaldehyde by Aqueous Alkalis HARALD HAMMARSTEN (*Annalen*, 1920, **420**, 262—275).—Th investigation forms part of a biochemical study of the fnnction o acetaldehyde in plants. Under the action of aqueous alkali, th aldehyde is decomposed into alcohol and acid, into aldol an aldehyde resin. The first and third types of action are chiefl described in the present communication.

The experiments were carried out with $N/2$-aqueous acet aldehyde solution at 0°, 18°, and 50° respectively. The bases use were the hydroxides of potassium, barium, calcium, and lead. I addition, buffer solutions prepared from the di- and monc hydrogen phosphates of potassium and sodium, and from borat and sodium hydroxide, were also employed. In the case of th alkali hydroxide solutions, the amount of acid formed was estimate by titration of the resulting solution with acid in the presence c phenolphthalein; with the buffer mixtures, the solutions wer strongly acidified with phosphoric acid, distilled to syrupy con sistency, and subsequently treated with steam until all acetic aci was removed, the latter being then titrated in the combined di tillate. Aldehyde resin was estimated by extraction of the solu tions with chloroform, evaporation of the latter, and desiccation c the residue at 120°/10 mm. until constant in weight.

The results are given in an extended series of tables. It i found that the aldol condensation proceeds at a relatively muc greater rate than the Cannizzaro reaction, the former taking plac

so rapidly that it is impossible for any considerable amounts of alcohol or acid to be formed. The maximum production of acid observed during the whole course of the experiments is only 12·5% of that theoretically possible. H. W.

Additive Compounds of the Acetylacetone Derivatives of the Rare Earths. G. JANTSCH and E. MEYER (*Ber.*, 1920, **53**, [*B*], 1577—1587. Compare Biltz and Clinch, A., 1904, i, 715.)—A series of additive compounds of the acetylacetone derivatives of the rare earths with ammonia, aniline, and pyridine has been investigated in the hope that a convenient chemical means of separating these elements might be found in their internally complex salts or their additive compounds. This does not, however, appear to be the case. The compounds which are described are considered to be constituted according to the annexed general formula.



Lanthanum acetylacetone, m. p. 151° (Biltz, *loc. cit.*, gives 183°), combines with a molecule of ammonia, pyridine, or aniline, respectively, to yield *compounds*, colourless needles, m. p. 147·5°, slender, colourless needles, m. p. 142°, and colourless, silky needles, m. p. 192°. *Lanthanum dibenzoylmethane*, pale yellow, shining needles, m. p. 141—143°, is obtained by the action of dibenzoylmethane on a suspension of lanthanum hydroxide in boiling ethyl alcohol; it combines with a molecule of ammonia, yielding a *substance*, pale yellow, slender needles, m. p. 99°, which rapidly loses the whole of the ammonia on exposure to air. Gadolinium acetylacetone is isolated in the form of the *dihydrate*, which, when crystallised from absolute alcohol, passes into the *monohydrate*, colourless, transparent needles, m. p. 142°; the *pyridine* compound, $Gd(C_5H_7O_2)_3,C_5H_5N$, forms colourless needles, m. p. 139·5°. *Yttrium acetylacetone*, colourless, transparent, pointed needles, m. p. 131°, is prepared in the same manner as the lanthanum salt, than which it is considerably more stable; the *compounds* with ammonia, pyridine, aniline, and acetonitrile form colourless needles, m. p. 129°, slender, shining needles, m. p. 121°, small needles, m. p. 109°, and colourless, fatty crystals, m. p. 138°; the first- and last-named compounds are somewhat unstable. *Yttrium dibenzoylmethane* forms long, yellow, shining needles, m. p. 240°; it does not appear to yield additive compounds with ammonia, pyridine, aniline, or acetonitrile. H. W.

Mutarotation of Dextrose in Alkaline Solution. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1920, **106**, 23—36).—The author has measured the velocities of disappearance of the mutarotation of dextrose in distilled water and in *N*/10—*N*/7000-sodium carbonate solutions, all the measurements being carried out at 20·4°. The values of the velocity constant of the change of mutarotation for different concentrations of sodium carbonate are: water, 7·11; *N*/7000, 7·32; *N*/6000, 9·32; *N*/5000, 12·70;

N/2000, 24·4; *N*/1000, 56·5; *N*/500, 93·1, these numbers giving almost exactly a straight line when plotted against the concentrations of the alkali (compare Osaka, A., 1909, i, 456).

T. H. P.

The Stability of α-Dextrose. Hans von Euler and Arvid Hedelius (*Biochem. Zeitsch.*, 1920, **107**, 150—158).—The H-ion concentration conducive to the maximum stability in the mutarotation of dextrose is $P_H = 3·6 \pm 0·2$. The temperature-coefficient at this H-ion concentration is only slightly higher than that at $P_H = 5$.

S. S. Z.

Action of the Carbonates of the Alkaline Earths on Dextrose. III. Hans Murschhauser (*Biochem. Zeitsch.*, 1919, **101**, 74—81. Compare this vol., i, 13, 662).—As in the case of calcium carbonate, strontium carbonate, barium carbonate, and magnesium carbonate when boiled with a solution of dextrose, gradually reduce the dextrorotation of the solution to zero or to slight lævorotation. The reduction of the sugar also falls, but to a smaller extent than the rotation. The formation of lævulose is established by the isolation of the phenylmethylosazone of this sugar from the treated solution. The fall in the reduction is ascribed to the formation of acids. The velocity of the change in the rotation is proportional to the equivalent weights of the dissolved substances.

S. S. Z.

Rate of Hydrolysis of Phosphoric Esters of Sugar Derivatives. P. A. Levene and M. Yamagawa (*J. Biol. Chem.*, 1920, **43**, 323—338).—There is much evidence that the ester derivatives of sugar may show considerable differences in the rate at which they are hydrolysed. The substances studied in this work were the phosphoric esters of (1) α-methylglucoside; (2) βγε-trimethyl methylglucoside; (3) α-, β-, γ-, ε-diacetoneglucose; (4) αβ-monoacetone-glucose; (5) a phosphoric acid ester of the same sugar derivative as in (4), but differing iu the position of the acid radicle; (6) ζ-benzoyl-αβ-monoacetone-glucose. The position of the phosphoric acid in the first compound is not known, but in (2) and (3) it is attached to the same carbon atom, so that these two compounds differ only in the nature of the substituent group. The fourth substance is formed as a by-product by the action of phosphoryl chloride on diacetone-glucose, and apparently contains the phosphoric acid radicle attached to a primary alcohol grouping, whereas the fifth substance is prepared by the action of phosphoryl chloride on monoacetone-glucose, and contains the phosphoric acid linked to a secondary alcohol group. The sixth substance differs from the preceding two by containing the phosphoric acid in a different position, by the number of the substituting groups, and by the difference in character of one of these groups.

The hydrolysis of these six substances was studied in approximately equivalent concentration, which was in the neighbourhood of

10%. The condition of hydrolysis consisted of treatment with 0·1*N*-sulphuric acid at 100°. The rate of hydrolysis followed the unimolecular law, and the following constants were obtained: K_1, 22(10⁻³); K_2, 43(10⁻³); K_3, 56(10⁻³); K_4, 44(10⁻³); K_5, 58(10⁻³); K_6, 18(10⁻³).

These results indicate that both the position of the phosphoric acid radicle and the character of the substituent groups exert an influence on the stability of the ester linking. J. C. D.

Crystalline Chlorotetra-acetyllævulose and Related Derivatives. D. H. Brauns (*J. Amer. Chem. Soc.*, 1920, **42**, 1846—1854).—β-Penta-acetyllævulose, when shaken in chloroform solution with aluminium chloride and phosphorus pentachloride, gives *chlorotetra-acetyllaevulose*, m. p. 83°, $[\alpha]_D^{20}$ −160·9°, which slowly decomposes in the air, giving tetra-acetyllævulose. By its general behaviour it is probable that this compound is an α-derivative. A better yield of the compound is obtained if the tetra-acetate is used instead of the penta-acetate, whilst if aluminium chloride is omitted in the preparation, the main product is *β-chlorotetra-acetyllaevulose*, m. p. 108°, $[\alpha]_D^{20}$ +45·3°. On ethylation, tetra-acetyllævulose gives *β-ethyltetra-acetyllaevulose*, m. p. 83°, $[\alpha]_D^{20}$ −127·6°. *β-Ethyl laevuloside*, m. p. 151°, $[\alpha]_D^{20}$ −155·3°, was obtained by the process previously described for β-methyl lævuloside (compare A., 1916, i, 547). Attempts to prepare α-methyl lævuloside by a biochemical method or by Fischer's method (compare A., 1895, ii, 553) were not successful. W. G.

Action of Different Catalysts on the Combustion of Burning Sucrose. J. Arvid Hedvall (*Svensk. Kem. Tidskr.*, 1920, **32**, 99—103; from *Chem. Zentr.*, 1920, iii, 337—338).—The author has extended the observations of Schade (*Münch. med. Woch.*, 1905, i, 1088) on the combustion of pieces of sucrose in air by distinguishing between the burning without formation of residue and that with the production of a porous mass, and by examining the effect of a large number of catalysts. The type of combustion first named is caused by strongly basic oxides and hydroxides, by certain oxides which are known to form complex organic compounds or to yield higher oxides transitorily, and by certain free metals. The formation of a residue occurs in the presence of free halogens, halogen hydracids, sulphuric acid, and certain other acids, and of many normal salts. H. W.

The Chemistry of Polysaccharides. The Preparation of Pure Polysaccharides. The Mode of Action of Diastatic Enzymes and the Dextrin Stage of Polysaccharides. E. Herzfeld and R. Klinger (*Biochem. Zeitsch.*, 1920, **107**, 268—294).—Pure starch was prepared by digesting fresh plant tissue with 33% sodium hydroxide on the water-bath, and by precipitating with 90% alcohol after centrifuging off the insoluble constituents. The precipitate was dissolved in water and repre-

cipitated with 90% alcohol, this being repeated twice; it was finally neutralised with hydrochloric acid, and precipitated again with alcohol. The same method was employed in the treatment of yeast, and the insoluble portion obtained by centrifuging the product from the first digestion of the yeast with the alkali was treated again with boiling alkali and alcohol, which yielded a cellulose-like substance. Cellulose was prepared from cotton wool by digesting it with strong sodium hydroxide and small quantities of carbon disulphide, centrifuging, and precipitating the viscous fluid with 90% alcohol. It was purified by reprecipitation with alcohol and neutralised with hydrochloric acid. Agar was purified by precipitating an alkaline solution of it with alcohol. Glycogen was obtained by digesting minced liver with 33% sodium hydroxide, and was purified by precipitation with alcohol. The properties of the polysaccharides prepared by the above methods were studied. The theory of the iodine reaction and of the action of diastatic enzymes as explained from considerations of the condition of the dispersed colloidal particles of the polysaccharides is discussed.

S. S. Z.

A Compound of Starch with Phosphoric Acid. JOHANNES KERB (*Biochem. Zeitsch.*, 1919, **100**, 3—14).—Starch was esterified with phosphoric acid by treating a soluble preparation with a solution of phosphoryl chloride in chloroform in the presence of calcium carbonate. The calcium salt of the amylophosphoric acid was precipitated with alcohol from the concentrated solution and purified. By means of diastatic cleavage, hexose monophosphoric acid was obtained from the compound in the form of a calcium salt. The latter substance was fermented by yeast. S. S. Z.

Preparation and Properties of a Highly-oxidised Cellulose. EDMUND KNECHT and LEONARD THOMPSON (*J. Soc. Dyers and Col.*, 1920, **36**, 251—255).—An improved method for preparing oxycellulose is carried out by treating filter paper with an acid solution of potassium permanganate (either one or two atoms of oxygen for each molecule of cellulose—$C_6H_{10}O_5$), washing the brown, disintegrated powder so formed, decolorising with hydrogen peroxide, and drying at 40°. In the stronger oxidation, the aldehyde group in the oxycellulose is not attacked. The method avoids the decomposition of oxycellulose by alkalis into non-reducing substances and its hydrolysis by acids. The so-formed oxycellulose gives an intense yellow colour with sodium hydroxide, and, on neutralisation, an acid cellulose having only slight reducing power is formed. It forms hydrazones with phenylhydrazine and *p*-nitrophenylhydrazine. On reduction, oxycellulose does not yield cellulose.

When kept for one day with cold 0·880 ammonia solution, a gelatinous mass is formed, which retains various amounts of ammonia on washing. Probably an unstable aldehyde–ammonia is formed. Oxycellulose does not react with aniline, but with hydrazine hydrate, hydroxylamine, and hydrogen cyanide it gives

indefinite compounds containing nitrogen. It reacts with sodium hydrogen sulphite solution.

Oxycellulose exerts its strongest reducing power in alkaline solution, and reduces solutions of cupric, silver and ferric salts. In the presence of sodium hydroxide, it readily reduces methylene-blue, safranine, rosinduline, indanthren, and indigotin.

It is not possible to estimate oxycellulose by means of its reaction with *p*-nitrophenylhydrazine, since absorption compounds are formed.

The new oxycellulose had a copper number of 14·2, as compared with 7·6 for Nastjukov's bleaching powder-oxycellulose.

A. J. H.

Picrates of the Nitrogen Bases of the Alcohol Radicles. A. RIES (*Zeitsch. Kryst. Min.*, 1920, **55**, 454—522. Compare T., 1909, **95**, 1275.)—Detailed crystallographic and optical data are given for thirty-one compounds, ranging from methylammonium picrate to tetra-*n*-propylammonium picrate. Many are dimorphous or trimorphous, whilst trimethyl*iso*propylammonium picrate is tetramorphous, and trimethyl*iso*butylammonium picrate is pentamorphous, namely, (1) monoclinic, D^{15} 1·378; (2) triclinic, D^{15} 1·378; (3) monoclinic-domatic, D^{15} 1·419; (4) triclinic, probably asymmetric, D^{15} 1·377; (5) hexagonal, D^{15} 1·377. Many are hexagonal or pseudo-hexagonal, or with prism-angles approaching 60°.

L. J. S.

Certain New Transformations of Ethylenediamine. WILHELM TRAUBE and ELISABETH PEISER (*Ber.*, 1920, **53**, [*B*], 1501—1508).—Aminoethylaminosulphonic acid (Traube and Brehmer, A., 1919, i, 434) has been converted into the corresponding nitroso-derivative, by the decomposition of which a series of hydroxy-, alkyloxy-, and halogeno-ethylamines has been prepared.

A well-cooled solution of β-aminoethylaminosulphonic acid in water is mixed with an aqueous solution of sodium nitrite, and subsequently acidified with dilute sulphuric acid, when *β-aminoethylnitrosoaminosulphonic acid*, $C_2H_4<{NH_3 \atop N(NO)\cdot SO_3}>$, separates in well-defined crystals, which are extremely explosive when dry (the moist preparations are used in the following experiments). The acid decomposes quantitatively in boiling aqueous solution in accordance with the equation $NH_2\cdot CH_2\cdot CH_2\cdot N(NO)\cdot SO_3H + H_2O = NH_2\cdot CH_2\cdot CH_2\cdot OH + N_2 + H_2SO_4$, and the β-aminoethyl alcohol was identified as the picrate, m. p. 159°, and picrolonate, m. p. 225° (decomp.). Concentrated hydrochloric acid converts the nitroso-acid into β-chloroethylamine (the *sulphate* was analysed), whilst hydrobromic acid acts with such violence that explosions readily occur, and gives β-bromoethylamine. *β-Fluoroethylamine*, obtained by treatment of the nitroso-acid with 40% hydrofluoric acid, evaporation of the solution, and distillation of the residue with steam after addition of an excess of alkali, has a strong odour

of ammonia, and is distinguished from the remaining halogeno-ethylamines by the much greater firmness with which the halogen atom is retained. The *hydrochloride*, *hydrobromide*, and *nitrate* are crystalline salts, but are not very characteristic by reason of their hygroscopic nature and ready solubility; the *picrolonate* crystallises in yellow, non-hygroscopic needles, m. p. 239°.

β-Aminoethyl methyl ether, colourless, mobile liquid, b. p. 95°/756 mm., is prepared from the nitroso-acid and boiling absolute methyl alcohol; the *hydrochloride*, hygroscopic crystals, and the *picrolonate*, yellow needles, m. p. 235°, are described. β-Aminodiethyl ether (picrolonate, m. p. 204°) is prepared in a similar manner. β-Aminoethyl methyl ether hydrochloride is transformed by potassium cyanate solution into *β-carbamidoethyl methyl ether*, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot OMe$, m. p. 63° after softening at 61°. The aqueous solution of the base reacts with phenylcarbimide to give *phenylcarbamidoethyl methyl ether*, m. p. 94·5°. *β-Aminoethyl* n-*propyl ether* was isolated in the form of its *picrolonate*, yellow, prismatic crystals, m. p. 188°, when rapidly heated.

The action of phenol on β-aminoethylnitrosoaminosulphonic acid leads to the formation of β-aminoethyl hydrogen sulphate instead of the expected aminoethyl phenyl ether. H. W.

Alkylimidodisulphonic Acids. WILHELM TRAUBE and MAX WOLFF (*Ber.*, 1920, **53**, [*B*], 1493—1501).—The investigation of the alkylation of basic potassium hydroxylaminedisulphonate (Traube, Ohlendorf, and Zander, this vol., i, 717) has been extended to basic potassium imidodisulphonate, $NK(SO_3K)_2$, which shows a somewhat similar behaviour, particularly towards the more active alkylating agents; with substances such as propyl iodide and benzyl chloride, the process is slower, the yields are poorer, and the products are mixed with potassium imidodisulphonate. The cause of this lies in the hydrolysis of the basic salt in aqueous solution, $NK(SO_3K)_2 + H_2O \rightleftharpoons NH(SO_3K)_2 + KOH$, and the dual nature of the process, which includes the alkylation of the basic salt and the decomposition of the alkyl haloid by free alkali; if the first process is slow and the second is comparatively rapid, equilibrium is so far disturbed by the removal of the alkali hydroxide that the normal salt is largely regenerated. Attempts to overcome this difficulty by working with concentrated solutions have not been particularly successful. The potassium alkylimidodisulphonates are readily decomposed by dilute acid into alkylamidosulphonates, which are then slowly converted into the corresponding primary amines.

Basic potassium imidodisulphonate is readily transformed by methyl sulphate or methyl iodide into *potassium methylimidodisulphonate*, $NMe(SO_3K)_2$, shining leaflets (the *lead*, *silver*, and *barium* salts dissolve freely in water), which is converted by very dilute sulphuric acid into *potassium methylamidosulphonate*, $NHMe\cdot SO_3K$, and by 25% hydrochloric acid into methylamine hydrochloride, the yield of the latter being 88% of that theoretically possible. Similarly, *potassium ethylimidodisulphonate*, long

needles, is converted into ethylamine (yield, 64%) and *potassium propylimidodisulphonate*, long, shining needles, into propylamine (yield about 40%). *Potassium epihydrinaminedisulphonate* is freely soluble in water.

Potassium ethylenediamine-NN'-tetrasulphonate,

$$C_2H_4[N(SO_3K)_2]_2,$$

small needles, is characterised by its sparing solubility in water, 100 c.c. of which dissolves only 0·2372 gram at the laboratory temperature (the *barium dipotassium* salt is practically insoluble in water). It is readily converted into *potassium ethylenediamine-NN'-disulphonate*, rectangular platelets, from which the corresponding free *acid*, shining leaflets, is obtained by means of perchloric acid, and, further, into ethylenediamine sulphate, the yield of the latter being 83% of that theoretically possible. H. W.

A New Method for Producing Hexamethylenetetramine. TH. SABALITSCHKA (*Zeitsch. angew. Chem.*, 1920, **33**, 217).—The formation of hexamethylenetetramine occurs, not only by the interaction of formaldehyde and free ammonia or ammonium carbonate, but also when a neutral ammonium salt, such as ammonium chloride, is employed in the absence of any alkali whatever. The quantitative aspect of the reaction in this case has not yet been investigated. G. F. M.

The Preparation of α-Derivatives of Hydroxylamine by means of Potassium Hydroxylaminedisulphonate. α-Methylhydroxylamine and αα-Ethylenedihydroxylamine. WILHELM TRAUBE, HEINRICH OHLENDORF, and HERBERT ZANDER (*Ber.*, 1920, **53**, [*B*], 1477—1492).—*Potassium α-methylhydroxylamine-ββ-disulphonate*, $OMe{\cdot}N(SO_3K)_2$, is readily obtained by shaking an aqueous solution of potassium hydroxylaminedisulphonate in the presence of that quantity of potassium hydroxide which is required to form the basic salt, $OK{\cdot}N(SO_3K)_2$, with methyl iodide, or, more rapidly, with methyl sulphate (the corresponding *lead*, *barium*, and *silver* salts are freely soluble in water), and is converted by being heated for a moment with dilute sulphuric acid into *α-methylhydroxylamine-β-sulphonic acid*, hygroscopic syrup, which is most readily isolated in the form of its *potassium* salt, well-formed, pearly plates (the *barium* salt, long, transparent prisms, $+1H_2O$, was analysed; the *lead* and *silver* salts are freely soluble in water). Protracted action of boiling sulphuric or hydrochloric acid on potassium methylhydroxylaminedisulphonate causes the elimination of both sulphonic groups and the formation of *α-methylhydroxylamine*, which is most readily isolated by adding an excess of alkali to the product of the action and distillation of the mixture with steam; the free base, b. p. 49—50°, is a colourless, mobile liquid with an amine-like odour. It reduces ammoniacal silver solution, but not Fehling's solution, at the ordinary temperature. The normal *sulphate*, m. p. 144°, the *nitrate*, large, transparent prisms, which detonate violently at

about 300°, and the *picrate*, m. p. 175°, are described. The base reacts with benzaldehyde to yield anti-*benzaldoxime* O-*methyl ether*, b. p. 191°, and with alloxan to give *methyl violurate*, m. p. 258—265°; it is converted by an aqueous solution of potassium cyanate into *methoxycarbamide*, m. p. 82—83°, by phenylthiocarbimide into N-*phenyl*-N′-*methoxythiocarbamide*, m. p. 116°, and by ethyl chloroformate into methoxyurethane, colourless oil, b. p. 186—188°. It combines with carbon disulphide to yield the very unstable *salt*, $OMe\cdot NH_2,HS\cdot CS\cdot NH\cdot OMe$, which was analysed in the form of the corresponding *silver* compound, $C_2H_3ONS_2Ag_2$, intensely yellow precipitate, which decomposes above 40°.

Potassium ethylhydroxylaminedisulphonate, well-formed clusters of needles, is considerably more slowly formed from basic potassium hydroxylaminedisulphonate than is the corresponding methyl derivative, and is converted successively into *potassium ethylhydroxylaminemonosulphonate*, shining needles, readily soluble in water (the *free acid* is hygroscopic), and ethylhydroxylamine hydrochloride, m. p. 126°. Epichlorohydrin and the basic sulphonate yield *potassium epihydrinhydroxylaminedisulphonate*, $\overset{O—}{\underset{CH_2}{|}}>CH\cdot CH_2\cdot O\cdot N(SO_3K)_2$, six-sided platelets. Similarly, ethylene dibromide gives *potassium αα′-ethylenedihydroxylaminetetrasulphonate*, $C_2H_4[O\cdot N(SO_3K)_2]_2$; the corresponding *silver* and *lead* salts are freely soluble in water, but a mixed *potassium barium* salt dissolves more sparingly. The tetrasulphonate is transformed successively into the very soluble *potassium αα′-ethylenedihydroxylaminedisulphonate* and into *αα′-ethylenedihydroxylamine*,

$$NH_2\cdot O\cdot CH_2\cdot CH_2\cdot O\cdot NH_2,$$

colourless liquid with a faint odour, b. p. 203°/atmospheric pressure (frequently accompanied by violent explosion), 105°/23 mm. It is only feebly alkaline in aqueous solution. The following derivatives are described: *sulphate*, m. p. 260°, which has an acid reaction in aqueous solution; *hydrochloride*, m. p. 233°; *nitrate*, m. p. 124°, which detonates when heated above its melting point; *biscarbamide*, $C_2H_4(O\cdot NH\cdot CO\cdot NH_2)_2$, colourless crystals, m. p. 190°; *bisphenylthiocarbamide*,

$$C_2H_4(O\cdot NH\cdot CS\cdot NHPh)_2,$$

m. p. 119°.

Basic potassium hydroxylaminedisulphonate reacts comparatively rapidly with benzenesulphonyl chloride, *potassium benzenesulphohydroxylaminedisulphonate*, $SO_2Ph\cdot O\cdot N(SO_3K)_2$, needles, moderately soluble in water being formed.

The action of cyanogen bromide or iodide on basic potassium hydroxylaminedisulphonate results in the formation of *potassium iminocarbonyldihydroxylaminetetrasulphonate*,

$$NH:C[O\cdot N(SO_3K)_2]_2,$$

small needles ($+2H_2O$); this salt is invariably produced when one molecular proportion of the cyanogen haloid is mixed with one or two molecular proportions of the salt, and appears to be formed by the condensation of a molecule of potassium cyanohydroxyl-

aminedisulphonate primarily produced with a further molecule of the basic salt. H. W.

Action of Diazomethane on Amino-acids. J. HERZIG and KARL LANDSTEINER (*Biochem. Zeitsch.*, 1920, **105**, 111—114).—The results of further experiments by Schuster (compare A., 1914, i, 753) show that Geake and Nierenstein's supposed proof of the betaine structure of the amino-acids (A., 1914, i, 1057) cannot be accepted as of general validity.

When glycine is treated with diazomethane, most of the former remains undissolved, the methoxyl value of the dissolved part being almost zero, and estimation of methylimide group giving a value only slightly above that obtained with glycine alone. Hippuric acid is converted mostly into the methyl ester. With alanine, which mostly remains undissolved, the soluble part contains 3·79% of methoxyl group. Phenylalanine and diazomethane yield an oil of the composition $CH_2Ph{\cdot}CH(NHMe){\cdot}CO_2Me$. These results and those obtained with leucine, glutamic acid, and tyrosine show that with only the two lowest amino-acids, glycine and alanine, diazomethane effects virtually no substitution, and that in either case introduction of a negative group into the molecule enhances the reactivity towards diazomethane. With the other amino-acids examined, a distinction must be made between substitution of the hydrogen of the carboxyl and amino-groups; substitution is almost complete in the former group, and takes place only with difficulty in the latter. The presence of free amino-acid is rendered probable by the reactivity of the carboxyl group, entry of the methyl residue at the nitrogen being possibly hindered by other unknown factors. According to Geake and Nierenstein's view, that absence of reactivity towards diazomethane in ethereal suspension constitutes a proof of the betaine structure of an amino-acid, such structure can be ascribed only to glycine and possibly to alanine, equilibrium between the betaine form and the ordinary form being assumed in other cases. The accuracy of Geake and Nierenstein's view is supported by the behaviour of glutamic acid. T. H. P.

Syntheses of β-Amino-acids from Substituted Ammonium Malonates and Formaldehyde. C. MANNICH and B. KATHER (*Ber.*, 1920, **53**, [*B*], 1368—1371).—The action of formaldehyde on aqueous solutions of the salts of malonic acid and amines leads to the formation of β-amino-acids, in accordance with the equation

$$CO_2H{\cdot}CHR{\cdot}CO_2H + NR_2'H + CH_2(OH)_2 = CO_2H{\cdot}CR(CH_2{\cdot}NR_2'){\cdot}CO_2H + 2H_2O.$$

The reaction is most successfully applied to monoalkylmalonic acids and secondary amines, since, in this case, each component only contains one replaceable hydrogen atom, and action can only proceed in one direction. Malonic acid contains two and ammonia three hydrogen atoms, all of which can react with formaldehyde, so that the product of the change is too complex to permit the isola-

tion of individual substances. In the condensation, the nitrogen atom invariably occupies the β-position to the carboxyl group. The action of heat on the β-aminodibasic acid results, in general, in the loss of carbon dioxide and amine, and the formation of an unsaturated acid.

ω-Dimethylaminodimethylmalonic acid,

$CO_2H\cdot CMe(CH_2\cdot NMe_2)\cdot CO_2H$,

from methylmalonic acid, dimethylamine, and formaldehyde, forms small prisms, m. p. about 98° (decomp.), and is decomposed by heat into carbon dioxide, dimethylamine, and methylacrylic acid. *Methyliminobisdimethylmalonic acid*,

$(CO_2H)_2CMe\cdot CH_2\cdot NMe\cdot CH_2\cdot CMe(CO_2H)_2$,

decomposes, with evolution of gas, at 83—84°, and cannot be preserved indefinitely at the ordinary temperature; it yields methylacrylic acid when heated. *ββ′-Tetramethyldiaminoisobutyric acid* (from malonic acid, dimethylamine, and formaldehyde), needles, m. p. 139°, forms a *dihydrochloride*, slender needles, m. p. 169°, which gives a sparingly soluble double salt with mercuric chloride. Formaldehyde and methylammonium malonate yield a complex mixture, from which an *aurichloride*, $C_5H_{10}O_2NAuCl_4$, was isolated with difficulty. H. W.

The Preparation of Guanidine by the Interaction of Dicyanodiamide and Ammonium Thiocvanate. EMIL ALPHONSE WERNER and JAMES BELL (T., 1920, **117**, 1133—1136).

Fixation of Labile, Hydrated Forms by means of Mercuric Cyanide. G. SCAGLIARINI and E. BONINI (*Gazzetta*, 1920, **50**, ii, 114—117).—Treatment of cobalt or nickel sulphate solution with mercuric cyanide solution yields the isomorphous double sulphates, $CoSO_4,Hg(CN)_2,10H_2O$ and $NiSO_4,Hg(CN)_2,10H_2O$, the former orange-red and the latter greenish-blue. By similar procedure the salts, $Co(NO_3)_2,Hg(CN)_2,6H_2O$ and $Ni(NO_3)_2,Hg(CN)_2,6H_2O$, may be obtained. When the complex cobalt sulphate is electrolysed in aqueous solution, the mercuric cyanide migrates to the cathode, and must hence be united, partly at least, to the cobalt atom (compare Kurnakov, A., 1898, ii, 475; Barbieri and Calzolari, A., 1911, i, 184, 266, 268). T. H. P.

Mercury Derivatives of Ethylene. W. MANCHOT and ARTHUR KLÜG (*Annalen*, 1920, **420**, 170—190).—The mercuration of ethylene has been described by Hofmann and Sand in a series of communications during the years 1900 and 1901, as the final result of which they are led to consider that two types of substances are produced, to which they assign the formulæ $OH\cdot CH_2\cdot CH_2\cdot HgX$ and $X\cdot Hg\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot HgX$ respectively. It has been shown, however, that the mercurated derivatives of acetylene are to be regarded as true acetylene derivatives (Manchot and Haas, A., 1913, i, 1009; Manchot and Mährlein, A., 1919, i, 145), and arguments are now advanced in favour of regarding the ethylenic compounds as additive substances, $C_2H_4,HgX\cdot OH$ and $2C_2H_4,O(HgX)_2$.

Hofmann and Sand's formula does not readily explain why their

compound is immediately decomposed by halogen acids with the violent evolution of acetylene, whereas it is stable towards other acids. According to the authors' experiments, a similar result is produced by the addition of potassium cyanide or potassium thiocyanate in the presence of acid. In general, the reaction is caused by all those substances which combine with mercuric haloids to yield additive compounds of the type $HgCl_2,2HCl$, and may be expressed by the equations: $C_2H_4,OH{\cdot}HgCl + HCl \rightleftharpoons C_2H_4,HgCl_2 + H_2O$ and $C_2H_4,HgCl_2 + 2HCl \rightleftharpoons HgCl_2,2HCl + C_2H_4$. In support of this hypothesis, it is shown that compounds of the type $HgX_2,2HX$ can be isolated, although with some difficulty, and that the most characteristic substance of this class is $Hg(SCN)_2,2HSCN$, and further that aqueous solutions of mercuric chloride readily absorb ethylene with ultimate disappearance of the ionic reactions of mercury, and that the absorption is very much less marked when hydrochloric acid is added to the mercuric chloride solution. Further, as is to be expected from the equation $C_2H_4,OH{\cdot}HgCl + NaCl \rightleftharpoons C_2H_4,HgCl_2 + NaOH$, decomposition of the additive compound can be effected by the addition of alkali haloids, but, in consequence of the back action, the effect is not very marked, and is most noticeable when potassium thiocyanate is employed.

It has been observed previously by Sand that the complex, $C_2H_4,Hg(OH){\cdot}$, behaves as a univalent radicle, and, in this connexion, the *dichromate*, $[C_2H_4,Hg(OH)]_2Cr_2O_7$, has now been prepared. The free *base*, $[C_2H_4,Hg(OH)]{\cdot}OH$, has also been isolated by the action of moist silver oxide on the corresponding bromide as a viscous mass which freely evolves ethylene on treatment with hydrochloric acid (the *platinichloride*, $[C_2H_4,Hg(OH)]_2PtCl_6,5H_2O$, was analysed). Contrary to the statement of Sand, the benzoyl derivative, $C_2H_4,Hg(OBz)I$, evolves ethylene when treated with hydrochloric acid, the comparative slowness of the action being due to the insolubility of the substance.

The decomposition of mercurated ethylene compounds by iodine is readily explained by the additive formula; the primary action consists in the displacement of oxygen by iodine (which is in accordance with the well-known properties of mercury salts), followed by addition of oxygen at the double bond, thus yielding $CH_2I{\cdot}CH_2{\cdot}OH$ and $O(CH_2{\cdot}CH_2I)_2$ respectively. The action of alkyl iodide lends further support to the additive hypothesis; according to Sand's formulation, the ethanol derivative, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}HgI$ should yield propyl alcohol when treated with methyl iodide, whereas it actually gives methyl alcohol, ethylene, and mercuric iodide. Similarly, the ethyl ether mercuri-salts yield ethylene in abundance when heated with methyl iodide at 110°, $2C_2H_4,HgI{\cdot}O{\cdot}HgI + 2CH_3I = 2C_2H_4 + 2HgI_2 + (CH_3)_2O$. H. W.

Relations between the Constitution and Physical Properties of Hydroaromatic Compounds. K. VON AUWERS (*Annalen*, 1920, **420**, 84—111. Compare A., 1916, i, 130—131).—**The present communication is mainly devoted to the *cyclo*hexanes.**

Since it is quite possible that stereoisomeric forms of these may be obtained according to the method of operation, they have in general been prepared according to a uniform scheme which starts from the requisite *cyclo*hexanol obtained by Sabatier's method. The secondary *cyclo*hexanols are converted into the iodides, and these are reduced to the hydrocarbons in accordance with Zelinski's method. The process is not readily applicable to tertiary *cyclo*hexanols, since unsaturated hydrocarbons are readily produced; in these cases it is preferable first to transform them by phosphorus pentachloride into the chloro-compounds and to reduce the latter by sodium in the presence of moist ether, the latter operation being performed as slowly as possible. The products invariably contain small amounts of unsaturated hydrocarbons, which are removed by the addition of a slight excess of bromine followed by distillation in a vacuum. The products are ultimately distilled over sodium, and must finally neither show Beilstein's halogen test nor be coloured by tetranitromethane.

The validity of the rules governing the relation between constitution and physical properties which were propounded previously (*loc. cit.*) has been confirmed for a series of compounds, and certain apparent exceptions have been removed. Experiments directed to explain these exceptions have shown that the hydrogenation of benzene derivatives may lead to the formation of different stereoisomeric forms of the corresponding hydroaromatic derivatives when different methods are employed, and that with simple derivatives of *cyclo*hexane the physical constants of stereoisomeric modifications may differ considerably.

The following compounds are described: 1 : 2-Dimethyl*cyclo*hexan-2-ol, b. p. 169°/ordinary pressure, 63—65°/9 mm., $D_4^{13\cdot7}$ 0·9252, D_4^{20} 0·920, $n_\alpha^{13\cdot7}$ 1·46035, $n_D^{13\cdot7}$ 1·46248, $n_\beta^{13\cdot7}$ 1·46848, $n_\gamma^{13\cdot7}$ 1·47330, n_D^{20} 1·4596; 2-*chloro*-1 : 2-*dimethyl*cyclo*hexane*, colourless oil, b. p. 53—54°/9 mm., $D_4^{13\cdot3}$ 0·9708, D_4^{20} 0·965, $n_\alpha^{13\cdot3}$ 1·46492, $n_D^{13\cdot3}$ 1·46723, $n_\beta^{13\cdot3}$ 1·47407, n_D^{20} 1·4642; 1 : 2-dimethyl*cyclo*hexane, b. p 35—37°/23 mm., 122·5—123·5°/760 mm. (?), $D_4^{17\cdot85}$ 0·7809, D_4^{20} 0 779, $n_\alpha^{17\cdot85}$ 1·42820, $n_D^{17\cdot85}$ 1·43020, $n_\beta^{17\cdot85}$ 1·43592, $n_\gamma^{17\cdot85}$ 1·44056, n_D^{20} 1·4292; 4-*chloro*-1 : 4-*dimethyl*cyclo*hexane*, b. p 50·5—52°/14 mm., $D_4^{18\cdot5}$ 0·9438, D_4^{20} 0·943, $n_\alpha^{18\cdot5}$ 1·45088, $n_D^{18\cdot5}$ 1·45372, $n_\beta^{18\cdot5}$ 1·45942, $n_\gamma^{18\cdot5}$ 1·46462, n_D^{20} 1·4530; 1 : 4-dimethyl*cyclo*hexane, b. p. 119·5—120·5°, $D_4^{15\cdot7}$ 0·7722, D_4^{20} 0·769, $n_\alpha^{15\cdot7}$ 1·42407, $n_D^{15\cdot7}$ 1·42597, $n_\beta^{15\cdot7}$ 1·43174, $n_\gamma^{15\cdot7}$ 1·43624, n_D^{20} 1·4240; 1 : 2-dimethyl*cyclo*hexan-4-ol, b. p. 188—188·5°, $D_4^{12\cdot5}$ 0·9118, D_4^{20} 0·906, $n_\alpha^{12\cdot5}$ 1·45826, $n_D^{12\cdot5}$ 1·46042, $n_\beta^{12\cdot5}$ 1·46645, $n_\gamma^{12\cdot6}$ 1·47121, n_D^{20} 1·4570; 1 : 4-*dimethyl*cyclo*hexan*-4-*one*, mobile oil, b. p. 187°, $D_4^{12\cdot6}$ 0·9121, D_4^{20} 0·906, $n_\alpha^{19\cdot6}$ 1·44871, $n_D^{12\cdot6}$ 1·45094, $n_\beta^{12\cdot6}$ 1·45712, $n_\gamma^{12\cdot6}$ 1·46208, n_D^{20} 1 4476 (a second specimen purified through the *semicarbazone*, needles, m. p. 189°, had $D_4^{12\cdot5}$ 0·9116, D_4^{20} 0·906, $n_\alpha^{12\cdot5}$ 1·44856, $n_D^{12\cdot5}$ 1·45068, $n_\beta^{12\cdot5}$ 1·45692, $n_\gamma^{12\cdot5}$ 1·46188, n_D^{20} 1·4473); a mixture of 1 : 2-*dimethyl*-Δ^3- and -Δ^4-cyclo*hexenes*, obtained by the action of anhydrous oxalic acid on 1 : 2-dimethyl*cyclo*hexan-4-ol, b. p. 123·5—124·5°, D_4^{20} 0·8059, n_α^{20} 1·44290, n_D^{20} 1·44529, n_β^{20} 1·45205, n_γ^{20} 1·45757; 5-*chloro*-1 : 3 : 5-*trimethyl*cyclo*hexane*, b. p. 53—53·5°/10 mm., $D_4^{13\cdot7}$ 0·9344 ($D_4^{13\cdot8}$ 0·9342)

D_4^{20} 0·929, $n_\alpha^{13\cdot9}$ 1·45566, $n_D^{13\cdot9}$ 1·45775, $n_\beta^{13\cdot9}$ 1·46412, $n_\gamma^{13\cdot9}$ 1·46925, n_D^{20} 1·4550; 1 : 3 : 5-trimethyl*cyclo*hexane, b. p. 137·5°, $D_4^{13\cdot1}$ 0·7777, D_4^{20} 0·772, $n_\alpha^{13\cdot1}$ 1·42971, $n_D^{13\cdot1}$ 1·43175, $n_\beta^{13\cdot1}$ 1·43764, $n_\gamma^{13\cdot1}$ 1·44235, n_D^{20} 1·4286; 1 : 2 : 5-*trimethyl*cyclo*hexan*-4-*ol*, viscous oil, b. p. 195—197°/760 mm. (?), 79—79·6°/10 mm., $D_4^{19\cdot2}$ 0·8988, D_4^{20} 0·898, $n_\alpha^{19\cdot2}$ 1·45639, $n_D^{19\cdot2}$ 1·45851, $n_\beta^{19\cdot2}$ 1·46459, $n_\gamma^{19\cdot2}$ 1·46938, n_D^{20} 1·4582; 1 : 2 : 5-*trimethyl*cyclo*hexan*-4-*one*, mobile oil, b. p. 195—196°, $D_4^{17\cdot4}$ 0·8989, D_4^{20} 0·897, $n_\alpha^{17\cdot4}$ 1·44797, $n_D^{17\cdot4}$ 1·45010, $n_\beta^{17\cdot4}$ 1·45618, $n_\gamma^{17\cdot4}$ 1·46112, n_D^{20} 1·4489 (a second preparation, purified through the *semicarbazone*, small needles, m. p. 175·5—176·5°, had b. p. 194—195°, $D_4^{14\cdot35}$ 0·8998, D_4^{20} 0·895, $n_\alpha^{14\cdot35}$ 1·44827, $n_D^{14\cdot35}$ 1·45039, $n_\beta^{14\cdot35}$ 1·45647, $n_\gamma^{14\cdot35}$ 1·46140, n_D^{20} 1·4479); 1 : 2 : 5-trimethyl*cyclo*hexane, b. p. 44—45°/12 mm., 140—141°/760 mm. (?), $D_4^{16\cdot9}$ 0·7799, D_4^{20} 0·778, $n_\alpha^{16\cdot9}$ 1·42860, $n_D^{16\cdot9}$ 1·43056, $n_\beta^{16\cdot9}$ 1·43632, $n_\gamma^{16\cdot9}$ 1·44099, n_D^{20} 1·4292; 1 : 2 : 5-*trimethyl*-Δ^4-cyclo*hexene*, obtained by the action of phosphoric oxide on 1 : 2 : 5-trimethyl*cyclo*hexan-4-ol and possibly containing a small proportion of 1 : 2 : 5-trimethyl-Δ^3-*cyclo*hexene, b. p. 144—146°, $D_4^{16\cdot15}$ 0·8078, D_4^{20} 0·805, $n_\alpha^{16\cdot15}$ 1·44742, $n_D^{16\cdot15}$ 1·44990, $n_\beta^{16\cdot15}$ 1·45683, $n_\gamma^{16\cdot15}$ 1·46264, n_D^{20} 1·4482; 1 : 2 : 4 : 5-*tetramethyl*cyclo*hexan*-4-*ol*, b. p. 83·2—86·8°/13 mm., 195—196°/760 mm. (?), $D_4^{16\cdot5}$ 0·8997, D_4^{20} 0·897, $n_\alpha^{16\cdot5}$ 1·45782, $n_D^{16\cdot5}$ 1·45999, $n_\beta^{16\cdot5}$ 1·46608, $n_\gamma^{16\cdot5}$ 1·47094, n_D^{20} 1·4584; 4-*chloro*-1 : 2 : 4 : 5-*tetramethyl*cyclo*hexane*, colourless oil, b. p. 69—71°/10 mm., $D_4^{13\cdot95}$ 0·9406, D_4^{20} 0·936, $n_\alpha^{13\cdot95}$ 1·46288, $n_D^{13\cdot95}$ 1·46515, $n_\beta^{13\cdot95}$ 1·47150, $n_\gamma^{13\cdot95}$ 1·47655, n_D^{20} 1·4624; 1 : 2 : 4 : 5-*tetramethyl*cyclo*hexane*, b. p. 160·5—161·5°, $D_4^{13\cdot1}$ 0·7910, D_4^{20} 0·785, $n_\alpha^{13\cdot1}$ 1·43517, $n_D^{13\cdot1}$ 1·43718, $n_\beta^{13\cdot1}$ 1·44307, $n_\gamma^{13\cdot1}$ 1·44772, n_D^{20} 1·4341; 1 : 2 : 4 : 5-*tetramethyl*-Δ^4-cyclo*hexene*, colourless oil, b. p. 165—167°, $D_4^{16\cdot5}$ 0·8199, D_4^{20} 0·817, $n_\alpha^{16\cdot5}$ 1·45617, $n_D^{16\cdot5}$ 1·45880, $n_\beta^{16\cdot5}$ 1·46597, $n_\gamma^{16\cdot5}$ 1·47192, n_D^{20} 1·4572; 1 : 1 : 3-trimethyl*cyclo*hexane, b. p. 137—138°, D_4^{25} 0·7868 ($D_4^{25\cdot3}$ 0·7866), D_4^{20} 0·790, $n_\alpha^{25\cdot3}$ 1·43177, $n_D^{25\cdot3}$ 1·43385, $n_\beta^{25\cdot3}$ 1·43998, $n_\gamma^{25\cdot3}$ 1·44453, n_D^{20} 1·4362; 1 : 1 : 3-trimethyl-Δ^2-*cyclo*hexen-4-one, b. p. 194—196°, $D_4^{16\cdot3}$ 0·9332, D_4^{20} 0·930, $n_\alpha^{16\cdot3}$ 1·47622, $n_D^{16\cdot3}$ 1·47951, $n_\beta^{16\cdot3}$ 1·48857, $n_\gamma^{16\cdot3}$ 1·49645, n_D^{20} 1·4779; 1 : 1 : 3-trimethyl*cyclo*hexan-4-one, b. p. 190—191°, $D_4^{16\cdot45}$ 0·9045, D_4^{20} 0·902, $n_\alpha^{16\cdot45}$ 1·44907, $n_D^{16\cdot45}$ 1·45130, $n_\beta^{16\cdot45}$ 1·45732, $n_\gamma^{16\cdot45}$ 1·46240, n_D^{20} 1·4497.

H. W.

Action of Chlorine on 3 : 5-Dichloro-1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene. LEONARD ERIC HINKEL (T., 1920, **117**, 1296—1303).

Process for the Reduction of Aromatic Nitro-compounds. JOSEPH TCHERNIAC and SAMUEL HENRY DAVIES (Brit. Pat. 150412).—Aromatic nitro-compounds, particularly hydroxynitro-compounds, are reduced by treatment with a mixture of hydriodic and hydrochloric acids. The consumption of iodine may be reduced to a minimum by adding a substance, such as phosphorus, which in presence of water reconverts the liberated iodine into hydriodic acid. In these circumstances it is obviously immaterial whether iodine or hydriodic acid is used in the first instance. For example, *p*-nitrophenol (139 parts) is reduced by boiling under a reflux condenser with 36 parts of amorphous phosphorus, 13·9 parts of

iodine, and 180 parts of 20% hydrochloric acid, until the vapour o iodine appears in the condenser. G. F. M.

The Synthesis of some Nitro-derivatives of Toluene OSCAR LISLE BRADY and PERCY NOEL WILLIAMS (T., 1920, **117** 1137—1140).

Binary Equilibria of certain Nitro-derivatives of Toluene M. GIUA (*Gazzetta*, 1920, **50**, ii, 101—113).—Bell and Herty (thi vol., i, 152) contradict the author's conclusion that molecular com pounds are formed in the three binary systems, *p*-nitrotoluene-2 : 4 : 6-trinitrotoluene, *p*-nitrotoluene–2 : 4-dinitrotoluene, and 2 : 4 dinitrotoluene–2 : 4 : 6-trinitrotoluene (A., 1914, i, 817). The autho refutes this contradiction, and gives further evidence in support o his conclusions. The experimental data obtained by Wogrinz and Vári (this vol., i, 307) also support the author's case. T. H. P.

Solubility and Crystallisation of Trinitro-*m*-xylene in Different Solvents. LOUIS DESVERGNES (*Ann. Chim. anal.*, 1920, [ii], **2**, 278—284).—The following quantities of trinitro-*m*-xylene are dissolved per 100 c.c. of solvent:—Ethyl alcohol at 15°, 0·09 gram; at 78°, 0·65 gram. Amyl alcohol at 15°, 0·14 gram; at 128°, 10·3 grams. Acetone at 15°, 0·95 gram; at 57°, 4·27 grams. Ethyl acetate at 15°, 0·77 gram; at 76°, 5·43 grams. Glacial acetic acid at 15°, 0·4 gram; at 115°, 15·03 grams. Nitric acid (D 1·500) at 15°, 5·51 grams; at 90°, 51·1 grams. Benzene at 15°, 0·92 gram; at 80°, 10·0 grams. Chlorobenzene at 15°, 1·06 grams; at 180° 108·58 grams. Nitrobenzene at 15°, 2·56 grams; at 90°, 19·60 grams. Carbon tetrachloride at 15°, 0·08 gram; at 75°, 0·96 gram. Toluene at 15°, 1·11 grams; at 110°, 21·7 grams. *m*-Xylene at 15° 0·83 gram; at 90°, 9·25 grams. The crystals obtained from these solutions are in the form of needles, m. p. 180·5—182·5°. The solubility in aniline at 15° is 3·87 grams per 100 c.c.; boiling aniline reacts with trinitro-*m*-xylene, yielding substances which have not yet been investigated. W. P. S.

***p*-Toluenesulphonyl Derivatives of Amino-acids.** TAKESABURO OSEKI (*J. Tokyo Chem. Soc.*, 1920, **41**, 8—19).—The following *p*-toluenesulphonyl derivatives have been prepared by shaking a solution of the amino-acid in the equivalent amount of alkali with an ethereal solution of *p*-toluenesulphonyl chloride for two hours, sodium hydroxide being frequently added to neutralise the hydrochloric acid formed in the reaction: the products are recrystallised after treatment with hydrochloric acid: of glycine, needles, m. p. 146°; of alanine, needles, m. p. 92—94°; of valine, m. p. 110—111°; of leucine, needles, m. p. 111·5°; of phenylalanine needles, m. p. 134—135°; of cystine, octahedra, m. p. 204—205°; of asparagine, m. p. 126—128°; of tyrosine, columns, m. p. 224—226° (this derivative does not give the Millon reaction, and

s insoluble in alkalis; by treatment with excess of hydrochloric acid it is converted into the derivative

$C_6H_4Me{\cdot}SO_2{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}SO_2{\cdot}C_6H_4Me$,

n. p. 117—119°); of tryptophan, needles, m. p. 176°; and of lysine and arginine, oils. CHEMICAL ABSTRACTS.

Mixed Crystals of 4 : 4′-Dichlorodiphenyl, 4 : 4′-Dibromodiphenyl, and 4 : 4′-Dimethyldiphenyl. K. MIELEITNER (*Zeitsch. Kryst. Min.*, 1920, **55**, 631—634).—Solutions in acetone of two of the compounds in variable proportions yielded measurable crystals with only a very limited range of miscibility in the case of the dichloro- and dibromo-compounds. The axial ratios (tabulated below) of the mixed crystals do not always lie between those of the corresponding pure compounds. An intimate interpenetration, rather than true isomorphous mixing, is therefore suggested.

Dichloro-. Per cent.	Dibromo-. Per cent.	Dimethyl-. Per cent.	*a*-axis.	*c*-axis.	D.
100·00	—	—	1·1569	0·7078	1·439
—	100·00	—	1·1181	0·6963	1·897
—	—	100·00	1·1722	0·7137	1·102
53·06	46·94	—	1·1278	0·6979	1·654
55·89	44·11	—	1·1316	0·6993	1·695
44·66	—	55·34	1·1504	0·7016	1·228
10·45	—	89·55	1·1802	0·7388	1·127
61·46	—	38·54	1·1571	0·7068	1·278
—	59·75	40·25	1·1416	0·6884	1·422

L. J. S.

Action of Amines on Trinitrophenylmethylnitroamine. THOMAS CAMPBELL JAMES, JAMES IVOR MORGAN JONES, and ROBERT ILLTYD LEWIS (T., 1920, **117**, 1273—1280).

New Syntheses of Hordenine. ERNST SPÄTH and PHILLIP SOBEL (*Monatsh.*, 1920, **41**, 77—90. Compare Barger, T., 1909, **105**, 2193; Rosenmund, A., *1910*, i, *241*; Léger, A., *1910*, i, *336*; Voswinckel, A., 1912, i, 443).—An ethereal solution of magnesium *p*-anisyl bromide is slowly added to dichlorodiethyl ether dissolved in ether at −15°, and the product, after being distilled under diminished pressure [b. p. 162—167°/16 mm. (decomp.)], is found to consist of a mixture of *β-chloro-α-*p*-methoxystyrlene*, $OMe{\cdot}C_6H_4{\cdot}CH{:}CHCl$, colourless liquid with an odour of aniseed, b. p. 137—140°/19 mm., and the desired *β-chloro-α-ethoxy-α-*p*-anisylethane*, $OMe{\cdot}C_6H_4{\cdot}CH(OEt){\cdot}CH_2Cl$, the latter having partly lost ethyl alcohol during the process of distillation. The undistilled product of the reaction is, however, converted by anhydrous dimethylamine into *β-dimethylamino-α-ethoxy-α-anisylethane*, $OMe{\cdot}C_6H_4{\cdot}CH(OEt){\cdot}CH_2{\cdot}NMe_2$, b. p. 152—153°/14 mm. (the *platinichloride* was analysed), which could not be satisfactorily converted into hordenine, since short treatment with hydriodic acid yielded a base which was not identical with hordenine, whilst pro-

by its direct synthesis from its components in aqueous-alcoholic solution. *3-Nitrodiethyl-*p*-toluidine-nitroform*, yellow crystals which decompose at 91°, is similarly converted into *3-nitrodiethyl-*p*-toluidine*, b. p. 101—102°/0·2 mm. *3-Nitrodimethyl-*p*-anisidine-nitroform*, yellow crystals which decompose at 108° after previous discoloration and can only be preserved for a few hours at the ordinary temperature, and *3-nitrodimethyl-*p*-anisidine*, b. p. 108—110°/0·5 mm., are prepared in like manner.

The action of an alcoholic solution of tetranitromethane on *p*-cresol dissolved in an ice-cold mixture of alcohol and pyridine yields *m*-nitro-*p*-cresol, m. p. 33·5°, b. p. 73—75°/0·5 mm., in 60% yield, and *pyridine nitroform*, which decomposes at 91—92° and cannot be long preserved unchanged at the ordinary temperature.

[With ADALBERT WAGNER.]—A solution of *iso*safrole in acetone and pyridine is converted by tetranitromethane dissolved in acetone into β-nitro*iso*safrole, m. p. 98° (compare Wallach and Müller, A., 1904, i, 754), the yield being 72·5% of that theoretically possible.

[With WILLY BÄJEN.]—Anethole is similarly transformed into β-nitroanethole, m. p. 48°, in 64·3% yield. H. W.

Tetranitromethane. III. Conversion of Tertiary Amines into Secondary Nitrosoamines. I. ERICH SCHMIDT and HEINRICH FISCHER (*Ber.*, 1920, **53**, [*B*], 1537—1544).—When tetranitromethane is allowed to act on a boiling alcoholic solution of a tertiary base in the presence of pyridine, the nitrating action of the liberated nitric acid (compare preceding abstract) is only slightly evident, the main change consisting in the removal of an N-alkyl group as the corresponding aldehyde and the formation of a secondary nitrosoamine: $:N{\cdot}CH_2R + C_5H_5N + (NO_2)_2C\overset{O}{\frown}N{\cdot}O{\cdot}NO_2 = :N{\cdot}NO + C_5H_5N,CH(NO_2)_3 + R{\cdot}CHO$. The action has so far been applied to fatty-aromatic amines, and does not appear to be influenced by the presence or position of further substituents in the ring. It is usually carried out in the following manner. An alcoholic solution of tetranitromethane (1·1 mol.) is slowly added to a boiling alcoholic solution of the tertiary amine (1 mol.) and pyridine (1·2—1·5 mol.), and ebullition is continued until the odour of tetranitromethane disappears. The mixture is poured into water and extracted with ether after addition of saturated salt solution. The ethereal solution is subjected to the action of steam in the presence of a further quantity of salt solution and a little potassium carbonate. Ether and the nitrosoamine are successively volatilised; the latter is freed from traces of pyridine by agitating its ethereal solution with dilute sulphuric acid, and subsequently purified in the usual manner. The following substances have been thus obtained: phenylmethylnitrosoamine, b. p. 86—87°/1·7 mm., and *p*-nitrophenylmethylnitrosoamine; phenylethylnitrosoamine, b. p. 96—97°/1·9 mm., and *p*-nitrophenylethylnitrosoamine; *o*-tolylmethylnitrosoamine, b. p. 89—90°/1·5 mm.; *o*-tolylethylnitrosoamine, b. p. 83—84°/0·6 mm.; *o*-chlorophenylmethylnitrosoamine, b. p. 89°/

1·2 mm.; *o*-anisylmethylnitrosoamine, b. p. 112°/1·1 mm., and *p*-nitro-*o*-anisylmethylnitrosoamine; m-*tolylmethylnitrosoamine*, orange-yellow oil, b. p. 89—90°/1 mm.; m-*chlorophenylmethylnitrosoamine*, nearly colourless leaflets, m. p. 36—37°; *p*-tolylmethylnitrosoamine, m. p. 52°, and 3-nitrodimethyl-*p*-toluidine; *p*-chlorophenylmethylnitrosoamine, m. p. 51°; p-*chlorophenylethylnitrosoamine*, colourless, interwoven needles, m. p. 60—61° (*p*-chlorodiethylaniline, which has been previously isolated by Hofmann in the crude condition, is obtained by the action of ethyl alcohol on *p*-chloroaniline hydrobromide at 150°, and forms colourless needles, m. p. 30°, b. p. 95—96°/1·5 mm.); *m*:4-xylylmethylnitrosoamine, pale yellow oil, b. p. 101°/1·3 mm. H. W.

Halogenalkylated Aromatic Amines. V. Preparation of Aryl Vinyl Ethers. JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1920, **53**, [*B*], 1399—1408).—The preparation of vinyl ethers is generally a matter of considerable difficulty, and few members of this class are known. The authors have therefore investigated a possible general method of synthesis which depends on (1) the replacement of the halogen atom of β-halogenalkylated aromatic amines by the radicle OR; (2) union of the basic ethers thus produced with methyl iodide or methyl sulphate; and (3) decomposition of the quaternary salts so formed with alkali in accordance with the scheme $RO\cdot[CH_2]_2\cdot NR_3'\cdot I + KOH \longrightarrow R\cdot O\cdot CH{:}CH_2 + NR_3$. Unfortunately, the process breaks down at the third stage, when R is an aliphatic residue, since the quaternary compounds are only decomposed with unusual difficulty, and are, in part, extensively changed and in part re-converted into the basic ether. With phenols, on the other hand, good results are obtained, and this is also the case with dihydroxy- and thio-phenols.

Peculiar interest attaches to the vinyl ethers from the point of view of the chemistry of perfumes, but the introduction of the vinyl complex is found to have a most irregular influence on the odour of the compounds produced.

N-β-*Naphthoxyethylmethylaniline*, $C_{10}H_7\cdot O\cdot[CH_2]_2\cdot NMePh$, m. p. 75°, b. p. 200—205°/mercury vacuum, is most readily prepared by heating β-naphthol with methylbromoethylaniline and potassium hydroxide in acetone solution. It is only feebly basic, but yields a *hydrochloride*, needles, m. p. 150°, a *platinichloride* decomposing at 128—129°, and a *methiodide*, m. p. 137°. Decomposition of the latter is best effected with boiling aqueous potassium hydroxide (15%), through which steam is blown continuously, whereby dimethylaniline and β-naphthyl vinyl ether are removed as soon as they are formed, whilst *N*-β-naphthoxyethylmethylaniline remains in the flask. The yield of the ether is 45—50% of that theoretically possible, whilst about a half of the original iodide is left as the corresponding base, which can be readily utilised for further preparations. β-*Naphthyl vinyl ether*, m. p. 63—64°, b. p. 137°/13 mm., has an intense odour of tangarine skins. In contrast to allyl ether (the same is true for all other representatives of this

class), it is not able to undergo the Claisen transformation into vinylated β-naphthol; the vinyl group does not unite with bromine smoothly, and is only very slowly and incompletely hydrogenated by Paal's method. The aromatic vinyl ethers are more stable towards hydrolysis than are the corresponding aliphatic compounds, and the odour of acetaldehyde is only apparent after protracted boiling with alkali hydroxide or dilute acid.

Carvacryloxyethylmethylaniline, $C_6H_3MePr\cdot O\cdot[CH_2]_2\cdot NMePh$, is a moderately viscous oil, b. p. 220—221°/11 mm., which yields a very soluble *picrate*, and an oily *hydrochloride* and *methiodide* (the *platinichloride* corresponding with the latter has m. p. 90°). *Carvacryl vinyl ether* has b. p. 217—218°/atmospheric pressure, and possesses an unpleasant odour dissimilar to that of the corresponding methyl or ethyl ether.

β-Tetrahydronaphthyloxyethylmethylaniline, b. p. 52—53°, b. p. 257—258°/14 mm., gives a *hydrochloride*, m. p. 163°, a *picrate*, m. p. 122°, and a *methiodide*, colourless, crystalline powder, m. p. 123°. *β-Tetrahydronaphthyl vinyl ether*, b. p. 121—122°/11 mm., has a faint, not unpleasant odour, which is less marked than that of the corresponding *allyl* ether, b. p. 158—161°/23 mm.

The action of methylbromoethylaniline on catechol leads to a mixture of *o-hydroxyphenoxyethylmethylaniline*, m. p. 71° (the *hydrochloride*, m. p. 195° after darkening above 140°, *picrate*, orange leaflets, m. p. 146°, *acetyl* derivative and *methiodide*, colourless leaflets, m. p. 135°, are described), and the symmetrical *bis-β-methylphenylaminoethyl ether of catechol*,

$$NMePh\cdot[CH_2]_2\cdot O\cdot C_6H_4\cdot O\cdot[CH_2]_2\cdot NMePh,$$

m. p. 90—91° (*hydrochloride*, *picrate*, yellow powder, m. p. 103°, *methiodide*, m. p. 96°). *Catechyl monovinyl ether*, b. p. 213°, is a colourless liquid with a faint odour. *Catechyl divinyl ether* has b. p. 206—209°.

Phenylthiolethylmethylaniline, $SPh\cdot[CH_2]_2\cdot NMePh$, almost odourless oil, b. p. 222—224°/14 mm. (*hydrochloride*, oily, *picrate*, yellow needles, m. p. 155°), yields an oily *methiodide* (the corresponding *platinichloride*, m. p. 155°, was analysed), which gives a 40% yield of *phenyl vinyl sulphide*, b. p. 200—201°, almost colourless liquid, which has a pleasant odour of radishes.

N-*Methyl-β-amyloxyethylaniline*, b. p. 154—156°/10 mm., is slowly formed in the usual manner; it yields oily salts and a non-crystalline *methiodide* (the corresponding *platinichloride* decomposes at 166° after darkening at 160°); when treated with potassium hydroxide, the quaternary iodide largely regenerates the original amine and only gives traces of a nitrogen-free oil with an ethereal odour.

N-*Methyl-β-thiocyanoethylaniline*, pale yellow oil, b. p. 186°/10 mm., is obtained with unusual ease from methyl-β-bromoethylaniline and potassium thiocyanate in aqueous-alcoholic solution, and yields a crystalline *methiodide*, m. p. 137—138°. The latter appears to be decomposed by potassium hydroxide primarily into dimethylaniline and *vinyl thiocyanate*; under the experimental conditions

adopted, however, the latter is unstable, and immediately decomposes in an undetermined direction. H. W.

Studies in Ring Formation. III. The Condensation of Aromatic Amines with α- and β-Diketones and with 4:4′-Diacetyldiphenyl. CLARENCE VICTOR FERRISS and EUSTACE EBENEZER TURNER (T., 1920, **117**, 1140—1151).

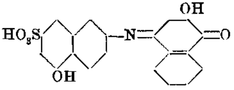
Influence of Substituents on Reactions. IV. Preferential Substitution Positions in β-Naphthylamine. HARTWIG FRANZEN and GUSTAV STÄUBLE (*J. pr. Chem.*, 1920, [ii], **101**, 58—74. Compare A., 1919, ii, 4).—It has been shown previously (Franzen and Aaslund, A., 1917, i, 644) that not more than three bromine atoms can be introduced readily into the β-naphthylamine molecule, forming successively 1-bromo-β-naphthylamine, 1:6-dibromo-β-naphthylamine (compare Claus and Philipson, A., 1891, 462), and a substance which has been considered by Claus and Jäck to be 1:4:6-tribromo-β-naphthylamine, but which is now shown to be the 1:3:6-derivative; this is deduced from the fact that the compound is converted by tin and hydrochloric acid into a dibromo-β-naphthylamine, which differs from the 1:6-derivative and after elimination of the amino-group yields 2:7-dibromonaphthalene. The authors are led to the conclusion that the positions 1, 6, and 3 are preferential substitution points in the bromination of β-naphthylamine; the β-amino-group has a much greater influence on the 1- than on the 6-hydrogen atom, whilst the latter is noticeably more influenced than the 3-hydrogen atom. The action of tin and hydrochloric acid on 1:6-dibromo-β-naphthylamine and 1:3:6-tribromo-β-naphthylamine leads essentially to the replacement of the 1-bromo-atom by hydrogen; in these two substances, the position 1 is a favoured substitution point with respect to hydrogen. In these cases also therefore, the substituent in position 1 is much more influenced by the amino-group than that in position 3 or 6.

α-Bromonaphthalene is not reduced by tin and hydrochloric acid. 1-Bromo-β-naphthylamine is converted by tin and hydrochloric acid or by stannous chloride into β-naphthylamine, but is not affected by alcoholic potassium hydroxide solution. 1:6-Dibromo-β-naphthylamine is transformed by tin and hydrochloric acid, by stannous chloride, by hydriodic acid or by cuprous chloride and hydrochloric acid into 6-bromo-β-naphthylamine, m. p. 128° (the hydrochloride, *acetyl* derivative, m. p. 192°, and *benzoyl* derivative, colourless leaflets, m. p. 218°, are described). 6-Bromo-β-naphthylamine is scarcely affected by tin and hydrochloric acid or by hydriodic acid. 1:3:6-Tribromo-β-naphthylamine is reduced by tin and hydrochloric acid to 3:6-*dibromo-β-naphthylamine*, small, colourless leaflets, m. p. 187° (*acetyl* derivative, long, slender needles, m. p. 195°, *benzoyl* derivative, long, silky needles, m. p. 161—162°); a similar result is obtained by the use of stannous chloride. H. W.

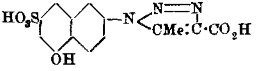
The Preparation of Thiocarbimides from Non-Aromatic Primary Bases. JULIUS VON BRAUN (*Ber.*, 1920, **53**, [*B*], 1588).—Thiocarbimides of non-aromatic primary bases are most conveniently prepared by the thiuram disulphide method (van Braun and Deutsch, A., 1912, i, 673), which is particularly applicable to the production of fatty-aromatic, hydroaromatic, and complex thiocarbimides. *cyclo*Hexylthiocarbimide (compare Skita and Rolfis, this vol., i, 607) is obtained quantitatively from *cyclo*hexylamine in this manner. H. W.

New Derivatives of *J*-acid [6-Amino-1-naphthol-3-sulphonic Acid]. W. KÖNIG and H. HALLER (*J. pr. Chem.*, 1920, [ii], **101**, 38—57).—The experiments were undertaken with the object of elucidating the causes which condition the peculiar tinctorial properties of derivatives of *J*-acid as compared with those derived from similar acids. In most of the work which has been accomplished previously, the alterations have been effected by alkylating, arylating, etc., the amino-group. The present communication describes the production of compounds obtained by replacement of the amino- by other radicles and by altering the sulphonic acid group; the consideration of the tinctorial properties of the substances is reserved for a subsequent paper. The following individual substances are described, which are generally prepared by well-known methods. In the case of the sulphonic acids, the *p*-toluidine salts have been investigated, since the free acids and the simple alkali salts are inconveniently freely soluble in water.

p-*Toluidine* 6-*iodo*-1-*naphthol*-3-*sulphonate*, pale pink leaflets; p-*toluidine* 6-*chloro*-1-*naphthol*-3-*sulphonate*, grey leaflets; p-*toluidine* 6-*azido*-1-*naphthol*-3-*sulphonate*, shining, transparent, colourless leaflets (the *disodium* salt is also described); 6-β-*hydroxynaphthaquinonimido*-1-*naphthol*-3-*sulphonic acid* (annexed formula), violet



powder; 6-*hydrazino*-1-*naphthol*-3-*sulphonic acid*, small, colourless needles; p-*toluidine* 6-*isatin*-1-*hydroxy*-2-*naphthylhydrazine*-3-*sulphonate*, lemon-yellow powder; 1(7′-*sulpho*-5′-*hydroxy*-2′-*naphthyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid* (annexed formula), colourless needles by the action of ethyl acetoacetate on *p*-toluidine 6-azido-1-naphthol-3-sulphonate in the presence of alcoholic sodium ethoxide, followed by hydrolysis



of the product with sodium hydroxide; *sodium* 5 : 5′-*dibenzoyloxy*-2 : 2′ : 1 : 1′-*dinaphthacarbazole*-7 : 7′-*disulphonate*; *sodium* 6-*benzoylamino*-1-*benzoxynaphthalene*-3-*sulphonate*, small, silky needles; 6-*benzoylamino*-1-*benzoyloxynaphthalene*-3-*sulphonyl chloride*, yel-

low glassy mass, m. p. 151°; the corresponding *anilide*, colourless crystals, m. p. 155°; *6-benzoylamino-a-naphthol-3-sulphonanilide* (from the dibenzoyl compound and dilute sodium hydroxide solution), pale yellow powder, m. p. 125°, which readily couples with diazotised *p*-toluidine to yield a pale red, monoazo-dye; *phenyl-2-benzoylamino-5-hydroxy-7-naphthylsulphone* (from the corresponding acid chloride, benzene, and aluminium chloride), pale yellow powder, which blackens without melting when heated.

In connexion with the conversion of *J*-acid by bisulphite into "carbazole *J*-acid," the mechanism of Bucherer's reaction is fully discussed; the author is led to the conclusion that the primary products are sulphurous esters, but the original paper must be consulted for details. H. W.

Alkali Fusions. II. Fusion of Sodium Benzene-*m*-disulphonate with Sodium Hydroxide for the Production of Resorcinol. MAX PHILLIPS and H. D. GIBBS (*J. Ind. Eng. Chem.*, 1920, **12**, 857—860).—The maximum yield of resorcinol is obtained by fusing 20 to 24 mols. of sodium hydroxide with 1 mol. of sodium benzene-*m*-disulphonate, but in practice the yields were nearly as good (60·1 to 63·5%) when only 16 mols. of alkali were used. The best temperature was 310°, and the time two honrs. At 330—350° there was some destruction of resorcinol, whilst at 270—290° the yields were lower, owing to the reaction being incomplete, and even by extending the time of fusion were not so good as at 310°. The presence of water in the fusion mixture reduces the yield of resorcinol, but does not make a very material difference if it does not exceed 2 to 4%. C. A. M.

Tautomerism of Phenols. Resorcinol. HANS TH. BUCHERER (*Ber.*, 1920, **53**, [*B*], 1457—1459).—The action of sodium hydrogen sulphite on a boiling aqueous solution of resorcinol slowly leads to the formation of a substance, $C_6H_9O_{11}S_3Na_3$, which has been regarded by Fuchs and Elsner (this vol., i, 545) as the sodium salt of the bisulphite compound of *cyclo*hexane 3:5-dionesulphonic acid. The stability of this compound towards boiling dilute mineral acids causes the author to doubt the constitution assigned to it and to consider it as allied to the sulphurous esters of mono- and di-hydric phenols, which he has shown to be characterised in this manner. It is further pointed out that Bucherer and Schenkel (A., 1908, i, 452) have obtained a compound, $C_5H_5N,3NaHSO_3,2H_2O$, from pyridine and bisulphite in which the pyridine nucleus is extensively altered, since the greater part of the pyridine nitrogen is readily liberated in the form of ammonia by cold dilute alkali; it therefore appears that cyclic systems with two or three molecules of bisulphite can be obtained readily and without the necessity of intervention of carbonyl groups. H. W.

Tautomerism of Resorcinol. J. HERZIG and S. ZEISEL (*Ber.*, 1920, **53**, [*B*], 1518).—In connexion with the recent publication

on this subject by Fuchs and Elsner (this vol., i, 545), the authors point out that they have conclusively proved the possibility of tautomerism in this substance by the action of potassium hydroxide and alkyl iodide. H. W.

Syntheses of Humic Acids. WILHELM ELLER and KÄTE KOCH (*Ber.*, 1920, **53**, [*B*], 1469—1476).—The oxidation of phenols in alkaline solution leads to the formation of substances which appear to be identical in all respects with the natural humic acids; only such phenols, however, as are capable of giving quinonoid intermediate products show this behaviour. The acids are obtained by allowing the alkaline solutions of the phenol to remain exposed to the air, or, more rapidly, by the addition of finely powdered potassium persulphate to the solution. The products from catechol, quinol, and *p*-benzoquinone give analytical figures in agreement with the formula $C_6H_4O_3$, but since the acids do not crystallise and cannot be purified by repeated precipitation, the purity of the substances can only be controlled by analysis of several independently prepared specimens. The synthetic substances are soluble in water and alcohol, and, to some extent, in ether, but this property is lost when they become dry. In proportion as they are washed free from mineral acid, they develop the power of forming colloidal solutions in water. The moist substances shrink greatly when dried, and at 100° lose water, forming hard, brittle masses, which are readily ground to a black, shining powder. Their alkali salts dissolve readily, the remaining salts very sparingly, in water. In these respects they behave exactly as do the natural humic acids, and the similarity also extends to their behaviour towards chlorine, nitric acid, sodium hypobromite, and acetic anhydride.

The humic acid obtained from phenol resembles the other synthetic products, except in its greater solubility in alcohol; it has, however, been so far impossible to obtain concordant analytical data for the product.

The work is considered to throw considerable light on the chemistry of the natural humic acids, since it proves definitely that a number of them are existant, and that the pure substances are free from nitrogen and are possessed of definite acidic properties (probably owing to the presence of an unchanged phenolic hydroxyl group). They are probably formed by elimination of water from the hexoses, with formation of quinones, $C_6H_{12}O_6 = 4H_2O + C_6H_4O_2$, and subsequent oxidation of the latter to humins; an experimental realisation of the first step in this hypothetical scheme has not yet been accomplished satisfactorily. H. W.

Diphenylene Sulphide in Coal Tar. O. KRUBER (*Ber.*, 1920, **53**, [*B*], 1566—1567. Compare Weissgerber and Kruber, this vol., i, 754).—The presence of diphenylene sulphide in crude phenanthrene (containing about 1% of sulphur) is established by

oxidising the latter with hydrogen peroxide in acetic acid solution, whereby diphenylenesulphone, m. p. 229—230°, is obtained.

H. W.

Diphenylaryltelluronium Salts. KARL LEDERER (*Ber.*, 1920, **53**, [*B*], 1430—1445. Compare A., 1916, i, 810; 1917, i, 134).—The preparation of the diphenylaryltelluronium salts is effected by the addition of the requisite Grignard reagent (two or, more usually, three times the calculated quantity is used) to a solution of diphenyltelluronium dichloride in dry toluene. The mixture is shaken and immediately treated with dilute hydrochloric acid, after which any residual solid is dissolved in boiling water. The solution is treated with potassium iodide in quantity sufficient to convert the telluronium salt into the iodide, when the latter separates, whilst a further quantity may be obtained by treatment of the filtrates with sulphurous acid, and subsequent concentration. It is frequently contaminated with basic iodide, in which case it is again dissolved in water, the solution is treated with acetic acid and potassium iodide, and subjected to protracted boiling, whereby the basic iodide is decomposed, with the separation of the di-iodide, which can readily be separated by filtration. The following series are described.

Diphenyl-p-*tolyltelluronium Salts.*—*Iodide*, colourless, crystalline powder, m. p. 219—220°; *bromide*, colourless needles, m. p. 228—229° after softening at 226°; *chloride*, partly crystalline mass; *picrate*, monoclinic prisms, m. p. 132—133° after softening at 130°; *mercuri-iodide*, microscopic needles, m. p. 222—223° after softening at 220°; *mercurichloride*, resinous mass.

Diphenyl-o-*tolyltelluronium Salts.*—*Iodide*, small crystals, m. p. 175—176° after softening at about 170° (*mercuri-iodide*, white, amorphous powder, which softens from about 154° and is completely melted at 184°); *chloride*, a resin; *mercurichloride*, colourless needles, m. p. 210—211° after softening at 207—208°; *bromide*, microscopic prisms, m. p. about 203° after softening at about 199°; *picrate*, small, triclinic crystals, m. p. 127—128° after softening at 122°.

Diphenyl-m-*tolyltelluronium Salts.*—*Iodide*, colourless needles, m. p. 190—191° (from water), 202° after softening at 200° (from alcohol); *mercuri-iodide*, cubic crystals from alcohol, m. p. 134—135° after softening at 132°, slender needles from glacial acetic acid, m. p. 132—133° after softening at 129°; the *chloride* and *mercurichloride* are resinous; *bromide*, needles, m. p. 202—203° after softening at 199° (*mercuribromide*, semi-solid mass); *picrate*, m. p. 105—106° after softening at 101°.

Triphenyltelluronium Salts.—*Iodide*, m. p. 247—248° after softening from 245°; *mercuri-iodide*, small, colourless plates, which darken at 146°, soften at 155°, and are molten at about 178°; *mercuribromide*, long, colourless needles, m. p. 143—144° (decomp.); *mercurichloride*, four-sided rods, m. p. 136—137° after softening at 130° (from water), slender, silky needles, m. p. 138—139° after softening at 135° (from glacial acetic acid).

Diphenyl-o-*xylyltelluronium iodide*, microscopic cubes (+2EtOH), m. p. 114—115° with effervescence. *Diphenyl*-m-*xylyltelluronium iodide*, colourless powder, m. p. about 103° after softening at 92°; *mercuri-iodide*, colourless powder, m. p. 201—202° after softening at 195°.

Diphenyl-p-*xylyltelluronium Salts.*—*Iodide*, m. p. 213—214° after softening at 211°; *mercuri-iodide*, yellow, amorphous powder, m. p. about 110° after softening at 100°; *chloride*, m. p. 210—211° after softening at 207°; *mercurichloride*, m. p. about 176° after softening at 172°; *bromide*, small crystals, m. p. 207—208° after softening at 204° (from water), rods, m. p. 220—221° after softening at 218° (from alcohol–ether); *mercuribromide*, needles, m. p. 178—180° after softening at 174° (from alcohol), 174—175° after softening at 166° (from glacial acetic acid); *picrate*, small, yellow, rhombic crystals, m. p. 170—171° after softening at 168°.

Diphenyl-p-*anisyltelluronium Salts.*—*Iodide*, small prisms (+0·5EtOH); *mercuri-iodide*, white, amorphous powder, m. p. 89—90° after softening at 86°; the *chloride*, *bromide*, and their *mercuric* double salts are oily or resinous; *picrate*, small, yellow, monoclinic crystals, m. p. 126—127° after softening at 125°.

Diphenyl-o-anisyltelluronium Salts.—*Iodide*, colourless crystals, m. p. 230—231° after softening at 226°; *mercuri-iodide*, colourless leaflets, m. p. 218—219° after softening at 215°; the *chloride* and *mercurichloride* are resinous; *bromide*, m. p. 220—221° after softening at 215°; *picrate*, m. p. 165—166° after softening at 160—161°.

Diphenyl-m-*anisyltelluronium iodide* was obtained as a white, crystalline powder, which softened at 85° and was completely melted at about 95°; it was not isolated in the pure condition.

Diphenyl-p-*phenetyltelluronium Salts.*—*Iodide*, crystalline powder, m. p. about 131° after softening at 125°; *mercuri-iodide*, white, amorphous powder, m. p. 76—77° after softening at 74°.

Diphenyl-o-*phenetyltelluronium Salts.*—*Iodide*, m. p. 247—248° (decomp.) after softening at 225°; *mercuri-iodide*, colourless crystals, which become yellow in sunlight, m. p. about 183—184° after softening at 174°; the *chloride*, *mercurichloride*, and *picrate* form wax-like masses; *bromide*, colourless, crystalline powder, m. p. 178—179° after softening at 174°.

Diphenyl-a-naphthyltelluronium Salts.—*Iodide*, m. p. about 148° after softening at 130°; *mercuri-iodide*, m. p. 126° after softening at 115°; the *chloride* and *bromide* could only be isolated in an impure state.

Diphenylmesityltelluronium iodide has m. p. 153—154° after softening at 152°, whilst the *mercuri-iodide* is a white powder, m. p. 93—94° after softening at about 89°. H. W.

Tautomerism in the Triarylcarbinols: Mono-*p*-hydroxydiphenyl-a-naphthylcarbinol. M. Gomberg and N. A. Lange (*J. Amer. Chem. Soc.*, 1920, **42**, 1879—1883. Compare following abstract).—*Phenyl-a-naphthyldichloromethane*, $C_{10}H_7{\cdot}CPhCl_2$, m. p.

92°, obtained by the action of phosphorus pentachloride on pheny α-naphthyl ketone, when slowly added in benzene solution to a boi ing solution of phenol in benzene gives *phenyl-α-naphthyldipher oxymethane*, $C_{10}H_7·CPh(OPh)_2$, m. p. 169—170°. If, howeve phenol and phenyl-α-naphthyldichloromethane react together a the ordinary temperature for twelve hours and then at 50° for on hour the product is the fuchsone *phenyl-α-naphthylquinomethan* $C_{10}H_7·CPh:C_6H_4:O$, m. p. 169—170°. If this fuchsone is boiled i alcoholic solution with aqueous sodium hydroxide until the colou of the solution has changed to a light yellow, and the solution i then diluted with water and saturated with ammonium chlorid *phenyl-p-hydroxyphenyl-α-naphthylcarbinol*,

$$C_{10}H_7·CPh(OH)·C_6H_4·OH,$$

is obtained in its quinonoid form, and it is not possible to isolat the benzenoid form. Thus, as in the case of its isomeride, dipheny 4-hydroxy-α-naphthylcarbinol (*loc. cit.*), the naphthyl group exert its tautomerising influence with the production of the quinonoi tautomeride.

When phenyl-α-naphthyldichloromethane and phenol previousl saturated with dry hydrogen chloride are heated at 110° for twent four hours and the product, after the removal of the excess o phenol by steam distillation, is poured into 5% aqueous sodium hydr oxide, *4 : 4′-dihydroxytriphenyl-α-naphthylmethane*,

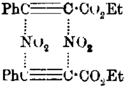
$$C_{10}H_7·CPh(C_6H_4·OH)_2,$$

m. p. 209—210° (decomp.), is obtained. W. G.

Tautomerism in the Triarylcarbinol Series; Diphenyl 4-hydroxy-1-naphthylcarbinol and Diphenyl-2-hydroxy 1-naphthylcarbinol. M. GOMBERG and F. W. SULLIVAN, jun (*J. Amer. Chem. Soc.*, 1920, **42**, 1864—1870).—A quantitative yiel of *p*-naphthafuchsone may be obtained by mixing together benz phenone chloride and α-naphthol in a dry atmosphere, and afte leaving the mixture overnight making it slightly alkaline wit dilute sodium hydroxide and distilling it with steam. On bromina tion in acetic acid solution the fuchsone gives *3-bromo-p-naphtha fuchsone*, m. p. 176°, and on chlorination *3-chloro-p-naphthafuch sone*, m. p. 161°. *o*-Naphthafuchsone was similarly obtained fron benzophenone chloride and β-naphthol, but in this case the addi tion of aluminium chloride as a catalyst was necessary. When dis solved in alcoholic sodium hydroxide and an aqueous solution o ammonium chloride added to this solution, *p*-naphthafuchsone gav almost entirely the quinonoid form of *diphenyl-4-hydroxy-α-naph thylcarbinol*, whilst *o*-naphthafuchsone gave exclusively th benzenoid form of *diphenyl-2-hydroxy-1-naphthylcarbinol*. Th bromo- and chloro-derivatives described above gave the quinonoi forms of *diphenyl-3-bromo-4-hydroxy-1-naphthylcarbinol* an *diphenyl-3-chloro-4-hydroxy-1-naphthylcarbinol* respectively.

Both *o*- and *p*-naphthafuchsones give additive compounds wit hydrogen chloride, but the chloro- and bromo-naphthafuchsones d not. W. G.

Addition of Nitrogen Peroxide to Ethyl Phenylpropiolate. HEINRICH WIELAND [with HANS WAGNER] (*Ber.*, 1920, **53**, [*B*], 1343—1346).—When nitrogen peroxide is passed into a cold solution of ethyl phenylpropiolate in light petroleum, colourless, prismatic crystals readily separate, which rapidly decompose into the original materials when filtered. Analysis of the compound is effected by the addition of an unweighed portion of the material to $N/10$-potassium hydroxide solution in the presence of ether and subsequent estimation of the ethyl phenylpropiolate and the amount of alkali used and of potassium nitrite formed. It is thus shown that one molecule of nitrogen peroxide is absorbed for each molecule of ester, and it is suggested that the molecules are united by means of the partial valencies of the acetylenic carbon atoms, as indicated by the annexed formula.



[With E. SCHAMBERG.]—When the primary labile additive compound is allowed to remain overnight in contact with light petroleum, it decomposes into ethyl phenylpropiolate and a mixture of the stereoisomeric ethyl αβ-dinitrocinnamates, of which the *modification*, almost colourless needles, m. p. 66·5°, has been isolated.

H. W.

Preparation of Tropic Acid from Ethyl Formylphenylacetate. JULIUS VON BRAUN (*Ber.*, 1920, **53**, [*B*], 1409).—Recently McKenzie and Wood (T., 1919, **115**, 228) have found that tropic acid can only be obtained in 16—30% yield by the reduction of ethyl formylphenylacetate with aluminium amalgam, and subsequent hydrolysis of the tropic ester. This result does not agree with the author's experience, since he finds the yield of acid to be about 50% of that theoretically possible, whilst a half of the original ester remains combined with the aluminium hydroxide, from which it can be recovered by acidification and extraction with ether. The difference is possibly to be ascribed to the use of insufficiently active aluminium amalgam.

H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXIX. Esterification of 4-Dimethylamino*iso*phthalic Acid. NIKOLA SMODLAKA (*Monatsh.*, 1920, **41**, 115—124. Compare Wegscheider, Malle, Ehrlich, and Skutezky, A., 1919, i, 76).—1-*Methyl 3-hydrogen 4-dimethylamino*isophthalate, colourless prisms or crystalline powder, m. p. 180°, is formed by the esterification of the acid with methyl-alcoholic hydrogen chloride at the ordinary temperature (preparative process) or by the hydrolysis of the normal ester in boiling aqueous methyl-alcoholic solution or with boiling $N/10$-hydrochloric acid (preparative method). 3-*Methyl 1-hydrogen 4-dimethylamino*isophthalate, colourless, shining leaflets, m. p. 190°, results from the esterification of the acid with methyl alcohol at 140°, from the action of methyl iodide on the normal silver or potassium hydrogen salt, and from the semi-hydrolysis of the normal

ester in methyl-alcoholic solution by means of potassium hydroxide or hydrogen chloride. The constitution of the esters is deduced from the production of the former by the esterification of the acid with methyl alcohol and hydrogen chloride, and from the behaviour of the silver salts when distilled, whereby in the first case a mixture of (?) *p*-dimethylaminobenzoic acid, m. p. 230—233°, and methyl *p*-dimethylaminobenzoate is produced, whilst in the second instance resinous and less definite substances are formed, which could not be fully examined owing to lack of material. The experiment, however, proves that the two silver salts behave in a totally dissimilar manner when heated, and that a transformation only occurs to a slight extent if at all. H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXX. Esterification of 4-Acetylamino*iso*phthalic Acid. HERMANN MEYER (*Monatsh.*, 1920, **41**, 125—138. Compare Wegscheider, Malle, Ehrlich, and Skutezky, A., 1919, i, 76, and preceding abstract).—1-Methyl 3-hydrogen 4-acetylamino*iso*phthalate, m. p. 218°, is prepared by the semi-hydrolysis of the normal ester with alkali in aqueous or methyl-alcoholic solution. The isomeric *3-methyl 1-hydrogen 4-acetylamino*isophthalate*, m. p. 265°, is obtained by the action of methyl iodide on the normal silver salt in the presence of methyl alcohol (the process does not, however, occur smoothly, and yields only 20% of the normal ester, a small amount of the hydrogen ester, and mainly the unchanged acid), or on the potassium hydrogen salt (in which case also side-reactions occur, giving rise to free acid). A hydrogen ester could not be isolated from the products of the action of methyl alcohol on the acid at 100° or 120—130° or 200°, since under these conditions loss of carbon dioxide appears to take place with consequent formation of *p*-acetylaminobenzoic acid. Similarly, the hydrogen ester could not be obtained by boiling the normal ester with dilute aqueous hydrochloric acid. The constitution of the esters follows from the observation that the isomeride, m. p. 218°, is transformed by boiling acetic anhydride into methyl anhydro-4-acetylamino*iso*phthalate, m. p. 172°, and since dehydration occurs by loss of water between the acetylamino- and the adjacent carboxyl group the ester must be the 1-methyl compound.

*Silver 4-acetylamino*isophthalate** forms a gelatinous mass; a silver hydrogen salt could not be isolated. *Potassium hydrogen 4-acetylamino*isophthalate** is prepared by the addition of aqueous potassium hydroxide solution to a suspension of the acid in methyl alcohol. H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXXI. Esterification of 4-Methylamino*iso*phthalic Acid. JOHANN TAUB (*Monatsh.*, 1920, **41**, 139—152. Compare Wegscheider, Malle, Ehrlich, and Skutezky, A., 1919, i, 76, and preceding abstracts).—1-Methyl 3-hydrogen 4-methylamino*iso*phthalate, colourless, delicate needles, m. p. 244—245° (decomp.), is formed in

ırger quantity than the isomeric *3-methyl 1-hydrogen 4-methyl-minoisophthalate* by all the methods of esterification and semi-ydrolysis; the latter, colourless crystals, m. p. 220—221°, is pre-ared by the semi-hydrolysis of the normal ester or by the action f methyl iodide on the silver salt. The former isomeride seems to e the only one produced by the action of methyl-alcoholic hydro-en chloride or sulphuric acid on the acid; in the absence of mineral cid, methyl alcohol only causes slight esterification of 4-methyl-minoisophthalic acid at 100°, whilst at 170° no trace of ester is roduced, the acid losing carbon dioxide and being converted into n anthraquinone dye, which was not further investigated. The ction of methyl iodide on the *potassium hydrogen* salt in the pres-nce of methyl alcohol yields mainly the acid, together with small uantities of the normal ester and the 1-methyl 3-hydrogen ester, hilst a mixture of acid, normal ester, 1- and 3-methyl hydrogen sters (in which the former considerably predominates), is obtained rom the *silver hydrogen* salt; the methylamino-group does not ppear to undergo methylation during this treatment. The hydro-ysis of the normal ester with methyl-alcoholic potassium hydroxide, queous potassium hydroxide, water, and with aqueous or methyl-lcoholic hydrochloric acid under varied conditions is described; in very case the hydrogen ester consists mainly of the 1-methyl com-ound, the 3-methyl isomeride being formed in subordinate amount at all. H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXXII. 4-Nitroisophthalic Acid and the Reduction of its Hydrogen Esters to 4-Aminoisophthalic Esters. PHILIPP AXER (*Monatsh.*, 1920, **41**, 153—165).—The oxidation of 4-nitro-*m*-ylene by calcium permanganate leads to the formation of a mix-ure of 4-nitroisophthalic acid, m. p. 255—256·5° (corr.), 6-nitro-*m*-oluic acid, yellow, silky needles, m. p. 218·5—219°, and small quan-ities of 4-nitro-*m*-toluic acid, m. p. 133—134·5°. *Potassium hydro-en 4-nitroisophthalate* is readily prepared as a white powder, spar-ıgly soluble in water, by the mixture of solutions of equivalent mounts of the normal potassium salt and the free acid; the silver ydrogen compound could not be prepared. *Methyl 4-nitroiso-hthalate*, yellow, rhombic crystals, $a:b:c=0·3875:0·3383:1$, m. p. 7—88·5°, is prepared in about 80% yield by the esterification of he acid with a mixture of equal volumes of concentrated sulphuric cid and methyl alcohol. *1-Methyl 3-hydrogen 4-nitroisophthalate*, ell-formed, colourless needles, m. p. 153·5—154° (corr.), is most onveniently prepared from the acid and methyl alcohol in the resence of a smaller proportion of concentrated sulphuric acid, nd its constitution is deduced from its mode of formation. It is lso obtained from the acid and methyl alcohol at 100° in the bsence of mineral acid. *3-Methyl 1-hydrogen 4-nitroisophthalate*, owder, m. p. 192—194° (corr.), is most conveniently prepared by he semi-hydrolysis of the normal ester either by potassium hydr-xide in aqueous methyl-alcoholic solution or by aqueous methyl-

alcoholic hydrogen chloride. Potassium hydrogen 4-nitro*iso*phthalate is not methylated by treatment with methyl iodide at 100° during twenty hours. The acid is partly transformed by methyl iodide in the presence of acetone and silver oxide into the normal ester, but remains unaffected by methyl sulphate. The silver salt is quantitatively transformed by methyl iodide into the normal ester.

1-Methyl 3-hydrogen 4-nitro*iso*phthalate is reduced by tin and concentrated hydrochloric acid to 1-methyl 3-hydrogen 4-amino*iso*phthalate, m. p. 221—222° (corr.), the yield, however, being poor, and the product contaminated with much free amino-acid. Better results are obtained with the isomeric ester, which yields *3-methyl 1-hydrogen 4-amino*iso*phthalate*, colourless, crystalline powder, m. p. 228—230° (corr., slight decomp.). Methyl 4-amino*iso*phthalate, m. p. 127—129° (corr.), is similarly obtained in good yield from the normal nitro-ester. H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXXIII. Esterification of Aminodicarboxylic Acids. RUDOLF WEGSCHEIDER (*Monatsh.*, 1920, **41**, 167—183).—A theoretical paper which is devoted to a discussion of the results obtained during the investigation of the esterification of aminocarboxylic acids and the partial hydrolysis of their esters.

The aminodicarboxylic acids and, so far as is known, other dicarboxylic acids which contain an imino-group or nitrogen atom as a member of an open chain generally conform to the rules which have been propounded for the formation of hydrogen esters. The amino-groups must be assumed to cause steric hindrance, the unsubstituted or alkylated amino-groups to have a positive and the acylated amino-groups to have a negative action. Less regularity is observed in the semi-hydrolysis; it not infrequently happens that the action follows different courses in alcoholic and aqueous solution, but, on the other hand, it is immaterial whether hydrolysis is effected by alkali hydroxide or by hydrochloric acid. In the semi-hydrolysis of the acylated amino-esters, the influence of the strength of the carboxyl group outweighs that of steric hindrance; on the other hand, these two factors do not appear adequate to explain the course of semi-hydrolysis of the esters of unsubstituted or *N*-alkylated amino-acids, particularly in aqueous solution. With regard to the other reactions, irregularities are only observed with dimethylamino*iso*phthalic acid (action of alcohol on the acid in the absence of catalyst and of methyl iodide on the salts). It is quite possible that all these irregularities (including such as are observed during semi-hydrolysis) are to be ascribed to the participation of the amino-groups in the reactions.

The following generalisations (which are not without exception) are drawn from a consideration of the melting points of amino-*iso*- and tere-phthalic acids and their esters: (1) Methylation at the nitrogen atom depresses the melting point (exceptions occur in the methylation of methylaminoterephthalic acid, 1-methyl

3-hydrogen 4-amino*iso*phthalate, and acetylamino*iso*phthalic acid). (2) Acetylation at the nitrogen atom raises the melting point of those hydrogen esters in which the esterified carboxyl is in the ortho-position to the amino-group, but depresses it in the case of the acids (except methylamino*iso*phthalic acid), and to a slight extent in that of the acid esters of different relative position, as well as in the instances of the dimethyl esters of amino*iso*phthalic acid and methylaminoterephthalic acid. (3) Derivatives of 4-amino*iso*phthalic acid have higher melting points than the corresponding compounds derived from aminoterephthalic acid. (The dimethyl esters of the amino- and acetylamino-acids form exceptions.) (4) Among isomeric hydrogen esters of acetylated acids, the compound in which the esterified carboxyl group is adjacent to the acetylamino-group has the higher melting point; a similar irregularity is not observed with the amino- and methylamino-acids. H. W.

Friedel and Crafts' Reaction: Nitrophthalic Anhydrides and Acetylaminophthalic Anhydrides with Benzene and Aluminium Chloride. WALTER A. LAWRANCE (*J. Amer. Chem. Soc.*, 1920, **42**, 1871—1879).—3-Nitrophthalic anhydride, when heated with benzene and aluminium chloride, gave a mixture of o'-*nitro*-o-*benzoylbenzoic acid*, m. p. 220—221° (decomp.), and m-*nitro*-o-*benzoylbenzoic acid*, m. p. 157—160° (decomp.). 2-Ethyl 1-hydrogen 3-nitrophthalate gave with thionyl chloride an *acid chloride*, m. p. 76—77°, which with benzene and aluminium chloride yielded *o*'-nitro-*o*-benzoylbenzoic acid. Similarly the *chloride* of 1-ethyl 2-hydrogen 3-nitrophthalate gave *m*-nitro-*o*-benzoylbenzoic acid. 4-Nitrophthalic anhydride when submitted to Friedel and Crafts' reaction gave *m*-nitro-*o*-benzoylbenzoic acid and *p*-nitro-*o*-benzoylbenzoic acid. Under similar conditions, 3-acetylaminophthalic anhydride yielded m-*amino*-o-*benzoylbenzoic acid*, m. p. 193—194°, and o'-*amino*-o-*benzoylbenzoic acid*, m. p. 159—160°, together with some *diphenyl-3-aminophthalide*, m. p. 86—89°. 4-Acetylaminophthalic anhydride gave *m*-amino-*o*-benzoylbenzoic acid and *p*-amino-*o*-benzoylbenzoic acid. W. G.

α-Naphtholphthaleins and its Ethers. W. SCHULENBERG (*Ber.*, 1920, **53**, [*B*], 1445—1457).—As considerable doubt exists as to the constitution of the α-naphtholphthalein obtained by the condensation of phthalyl chloride with α-naphthol (compare Sörensen and Palitzsch, A., 1910, ii, 446; Copisarow and Weizmann, T., 1915, **107**, 878; Csányi, this vol., i, 54), the author has attempted the synthesis of an undoubted *oo*'-naphtholphthalein, and for this purpose has condensed α-naphtholphthaloylic acid (Deichler and Weizmann, A., 1903, i, 349) with α-naphthol in sulphuric acid solution; the product forms colourless crystals, m. p. 253—254° after previous darkening, and closely resembles the substance described by Csányi as the *pp*'-isomeride, but differs widely from the *oo*'-derivative described by Copisarow and Weizmann, to which the m. p. 209—210° is ascribed. The mode of attachment of the second naphthol group is elucidated by the conversion of

the substance into α-naphthafluoran. The same substance was also obtained in small yield by the interaction of phthalyl chloride and α-naphthol under milder conditions than those usually adopted, whilst no trace of an isomeric *p*-phthalein could be detected.

The condensation of phthalic acid with α-naphthyl ethers follows a different course. Thus phthalic anhydride and α-naphthyl methyl ether react in carbon disulphide solution in the presence of aluminium chloride to yield 4-*methoxynaphthylphthaloylic acid*, colourless, acute prisms, m. p. 194° (the *sodium* salt, rhombic plates, and *calcium* salt, prisms, $+10H_2O$, are described), which can also be prepared from phthalyl chloride and α-naphthyl methyl ether. The constitution of the acid is deduced from the extreme difficulty of effecting its demethylation, and, with greater certainty, from a comparison of its properties with those of the isomeric acid of the ortho-series. Thus the former yields a *normal* and a *pseudo-methyl* ester, colourless, rhombic plates, m. p. 96°, and needles m. p. 120°, whilst the latter gives an *ether* ester, double pyramids m. p. 117—119°, and an *ether acid*, colourless needles, m. p. 179°. Finally, when melted with potassium hydroxide, the acid yields 1:4-hydroxynaphthoic acid, m. p. 178°. 4-Methoxynaphthylphthaloylic acid behaves as a weak acid, and is partly liberated from its sodium salt by carbon dioxide, and cannot be titrated with sodium hydroxide in the presence of phenolphthalein as indicator: its behaviour indicates its existence in the desmotropic forms, $CO_2H\cdot C_6H_4\cdot CO\cdot C_{10}H_6\cdot OMe$ and

$$C_6H_4{<}{\overset{C(OH)\cdot C_{10}H_6(OMe)}{\underset{CO}{}}}{>}O,$$

and this conception is supported by the isolation of the two methyl esters mentioned above. It suffers extensive decomposition when heated above its melting point, yielding, among other substances α-naphthyl methyl ether, phthalic acid, α-naphthafluoran, and a substance, pale yellow, hexagonal prisms, m. p. 201—202°, which was not further identified. It condenses with α-naphthyl methyl ether in the presence of concentrated sulphuric acid to give p-*naphtholphthalein dimethyl ether*, colourless, slender needles, m. p. 246—247°, which can also be obtained in 83% yield by the prolonged interaction of phthalyl chloride and α-naphthyl methyl ether in carbon disulphide solution in the presence of a trace of aluminium chloride at the ordinary temperature. The isomeric o-*naphtholphthalein dimethyl ether* is prepared by methylation of the phthalein, and forms colourless, microscopic needles, m. p. 291°.

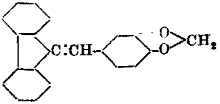
The results outlined above do not appear to harmonise readily with those obtained by Conisarow and Weizmann (*loc. cit.*), who find that the action of phthalyl chloride on α-naphthyl ethyl ether produces successively o-1-ethoxynaphthoylbenzoic acid, m. p. 155—156°, and di-1-ethoxynaphthylphthalide, m. p. 159°. The author has therefore repeated the work, and has obtained totally different results, since he finds the acid to melt at 166—167° and to have all the properties of a para-derivative, since it behaves

towards concentrated sulphuric acid in precisely the same manner as 4-methoxynaphthylphthaloylic acid, and is converted by fused potassium hydroxide into 4-hydroxynaphthoic acid. Further, the naphtholphthalein ethyl ether did not melt below 298°, whilst the acid was indifferent towards dealkylating agents. 1:2-Naphtholphthaloylic acid can be readily converted into o-1-*ethoxynaphthoylbenzoic acid*, irregular prisms, m. p. 145°, by *treatment with ethyl sulphate and subsequent hydrolysis of the ethyl* ester, prisms, m. p. 89°, thus produced. H. W.

Synthesis of 3 : 5-Dihydroxybenzaldehyde. F. MAUTHNER (*J. pr. Chem.*, 1920, [ii], **101**, 93—96).—3:5-*Dimethylcarbonato-benzaldehyde*, m. p. 154—155°, is prepared by the action of hydrogen on a solution of 3:5-dimethylcarbonatobenzoyl chloride (E. and H. O. L. Fischer, A., 1913, i, 478) in dry toluene at 110° in the presence of palladised barium sulphate. It yields a p-*nitrophenylhydrazone*, red needles, m. p. 222—223°, and is converted by aqueous sodium hydroxide and subsequent acidification into 3:5-*dihydroxybenzaldehyde*, colourless needles, m. p. 145—146°; the p-*nitrophenylhydrazone*, which completely decomposes, without melting, at 280°, and the *semicarbazone*, long needles, m. p. 223—224° (decomp.), of the latter are described. H. W.

Preparation of Piperonaldehyde from Camphor Oil. I. and II. SHOICHIRO NAGAI (*J. Chem. Ind. Tokyo*, 1920, **23**, 56—79, 151—172).—The fraction of camphor oil, b. p. 220—230°, contains mainly safrole, eugenol, carvacrol, cadinene, and *n*-octoic acid. By further distillation of this fraction, treatment with 25% *sodium* hydroxide, *cooling at* −19°, *and adding a few crystals of* safrole, safrole could be completely crystallised out. Next, when 300 c.c. of safrole are heated with 45 grams of potassium hydroxide (15 grams in each 100 c.c.) for five hours at 180—200°, 90% was changed into *iso*safrole. The method of oxidation of *iso*safrole into piperonaldehyde is discussed. Potassium dichromate and sulphuric acid gave the best yield, 47% of the theoretical value. When *potassium permanganate was used, the yield was only 8%, most of* the *iso*safrole being oxidised to piperonylic acid. The purification of piperonaldehyde is best effected by recrystallisation from 70% alcohol. CHEMICAL ABSTRACTS.

New Reaction of Aldehydes. REMO DE FAZI (*Gazzetta*, 1920, **50**, ii, 146—148. Compare A., 1916, ii, 457; Guglialmelli and Delmon, A., 1918, i, 161).—Since fluorene resembles acenaphthene in giving a reddish-violet coloration with cyclic aldehydes in presence of concentrated sulphuric acid, the author has initiated experiments to ascertain if the condensation products of fluorene with aldehydes are able to yield this coloration with the sulphuric acid. It is



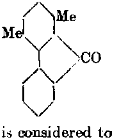
found that, in presence of sodium ethoxide, fluorene condenses at the ordinary temperature with piperonaldehyde, *m*-tolualdehyde, cuminaldehyde, *p*-dimethylaminobenzaldehyde, etc.; for instance, with piperonaldehyde, fluorene yields piperonylidenefluorene (foregoing formula). These condensation products, to be described in detail later, give the above coloration in alcoholic solution with concentrated sulphuric acid. T. H. P.

Constitution of the Salts of Aminoacetophenones. MITSURU KUHARA, HEIKICHI SAITO, and AKIRA SHIMOMURA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 201—215).—A study of the absorption spectra of the different salts of the three isomeric aminoacetophenones. The hydrochlorides of *o*- and *p*-aminoacetophenones both give coloured solutions in alcohol, and these coloured salts show a new absorption band in the visible region. This coloration is weakened if an excess of dry hydrogen chloride is passed through the alcoholic solution, and then the second band is no longer visible. *m*-Aminoacetophenone hydrochloride and *p*-dimethylaminoacetophenone hydrochloride do not give coloured salts, and their alcoholic solutions do not give an extra absorption band. It is considered that the coloured ortho- and para-salts are the quinonoid form and the colourless salts the benzenoid form, the change from one form to the other being of the keto-enol type.

p-Dimethylaminoacetophenone, m. p. 105°, was prepared by heating *p*-aminoacetophenone and methyl iodide in aqueous sodium hydroxide for several hours. It gave a *hydrochloride*, m. p. 147—148° (decomp.), and a *picrate*, m. p. 124° (decomp.). W. G.

Preparation of 1 : 4-Dimethylfluorenone and Attempts to Transform it into a Derivative of Phenanthrone. ALFRED SCHAARSCHMIDT and JOHANN HERZENBERG (*Ber.*, 1920, **53**, [*B*], 1388—1398. Compare Schaarschmidt, A., 1917, i, 275). —Various attempts to synthesise *o*-aminophenyl *p*-xylyl ketone are described. Thus, 2-p-*toluenesulphonylaminophenyl* p-*xylyl ketone*, $C_6H_3Me_2\cdot CO\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_6H_4Me$, small, colourless crystals, m. p. 107—108°, was prepared by the successive action of phosphorus pentachloride and aluminium chloride on *p*-toluenesulphonylanthranilic acid in the presence of *p*-xylene, but the *p*-toluenesulphonyl group could not be smoothly removed. Similarly, *p*-xyloyl-*o*-benzoic acid was converted successively into the chloride and *amide*, colourless needles, m. p. 149—150°, which could not be transformed into the amine in a satisfactory manner. Attempts to prepare *o*-nitrophenyl *p*-xylyl ketone by the action of *o*-nitrobenzoyl chloride on *p*-xylene in the presence of aluminium chloride and carbon disulphide were unsuccessful, resinous products being obtained. Finally, o-*bromophenyl* p-*xylyl ketone*, colourless, shining leaflets, m. p. 46°, was converted by alcoholic ammonia at 180—190° into *o-aminophenyl* p-*xylyl ketone*, mainly obtained as a yellow oil which decomposed completely when distilled; from

this, however, small amounts of pale yellow crystals, m. p. 76—78° to a cloudy liquid, which suddenly became transparent at 88—90°, could be isolated. It was converted by diazotisation and subsequent treatment with copper powder into *o-hydroxyphenyl* p-*xylyl ketone* (yellowish-brown, viscous mass, which was not further investigated), 2:5-dimethylbenzophenone, b. p. 312—314°/atmospheric pressure, and 1:4-*dimethylfluorenone* (annexed formula), long, yellow needles, m. p. 108°. When fused with potassium hydroxide, the latter yields an *acid*, colourless needles, m. p. 145° (the *silver* salt is described), which, since it is not esterified by cold saturated methyl-alcoholic hydrogen chloride, and yields 1:4-dimethylfluorenone when treated with concentrated sulphuric acid, is considered to be 2:5-dimethyldiphenyl-6-carboxylic acid.



The fission of substituted ring ketones under the influence of molten alkali hydroxide appears to take place quantitatively in one direction only, and the position occupied by the carboxyl group depends on the substituent already present. If the latter is acidic in character, the new carboxyl group becomes located in the unsubstituted benzene nucleus; if, however, it is basic ($-NH_2$ or $-OH$), the new group is attached to the already substituted nucleus. The latter seems also to be the case when a methyl radicle is in the ortho-position. H. W.

Anthracene. VI. Desmotropy of the Reduction Products of Hydroxyanthraquinones. KURT H. MEYER and ALBERT SANDER (*Annalen*, 1920, **420**, 113—125. Compare A., 1911, i, 193).—An investigation of the effect of the introduction of hydroxy-groups on the equilibrium between anthrone and anthranol forms.

The reduction of 1-hydroxyanthraquinone to a substance considered to be 1-hydroxyanthranol has been described by the Höchst Farbwerke (D.R.-P. 242053); the absence of fluorescence from the alcoholic solution and failure of the substance to combine with bromine show it to be in reality 1-hydroxyanthrone, and this conception explains the observed ability of the compound to condense with isatin chloride or anilide, with the production of indigoid dyes containing the new group in the side nucleus. In alcoholic solution, equilibrium is attained in the presence of 3—4% of hydroxyanthranol. With 1:9-dihydroxyanthrone and 1-hydroxyanthraquinol, equilibrium is set up when about 10% of the latter is present. In the cases of 1:4-dihydroxyoxanthrone and 1:4-dihydroxyanthraquinol, the latter is found to pass with great readiness into the former, so that it appears, in general, that the tendency towards ketone formation is increased by the entrance of hydroxyl groups in the α-position in the side nucleus.

The following individual substances are described: 1:9-*anthranylene diacetate*, $C_6H_4<^{C(OAc)}_{CH}>C_6H_3(OAc)$, colourless or pale yellow needles, m. p. 148—149°; the *dibenzoate*, yellow

*f f**

needles, m. p. 191° (from α-hydroxyanthrone and the requisite acid chloride in the presence of pyridine); 9-*bromo*-1-*hydroxyanthrone*, $C_6H_4<^{-CO-}_{CHBr}>C_6H_3\cdot OH$, yellow needles, m. p. 273° (decomp.) after softening and darkening from 130°, which readily loses hydrogen bromide, and, on treatment with copper powder, gave a *substance*, m. p. 188—189°; 1:9-*dihydroxyanthrone*, $C_6H_4<^{-CO-}_{CH(OH)}>C_6H_3\cdot OH$, deep yellow needles, m. p. 135—137° (from the bromo-compound and aqueous acetone); 1-*hydroxyanthraquinol*, dark olive-green needles, m. p. 204—206°, which undergoes autoxidation with extreme ease; 1:4:9-trihydroxyanthrone, $C_6H_4<^{-CO-}_{CH(OH)}>C_6H_2(OH)_2$, m. p. 157—158° after previous softening, which is best obtained by reducing a solution of quinizarin in glacial acetic acid with tin and hydrochloric acid, and which has been considered by Liebermann to be 1:4-dihydroxyanthraquinol; the latter *substance*, prepared by reduction of quinizarin with zinc dust in alkaline solution and subsequent acidification, has m. p. 131—136°, readily undergoes autoxidation, passes into the ketonic form when recrystallisation is attempted, and is oxidised by an alcoholic solution of bromine to quinizarin.

Purpurin, when subjected to reduction, is converted into leucopurpurin and a substance, $C_{14}H_{10}O_5$, m. p. 162—163°, which is transformed in alkaline solution into quinizarin, and has hence been termed leucoquinizarin I. It is now shown that it is produced when leucopurpurin is boiled in acetic acid solution, that it is stable towards air and indifferent to an alcoholic solution of bromine, and, further, that its conversion into quinizarin by sodium hydroxide occurs in complete absence of air. It therefore appears to be 2-hydroxy-1:4-diketo-1:2:3:4-tetrahydroanthraquinol, and to be formed by the passage of leucopurpurin into the ketonic form, the subsequent production of quinizarin being due to the loss of water.

Liebermann's β-hydroxyanthranol has been further examined, but definite conclusions as to the desmotropic relationships cannot yet be drawn; the stable modification, however, appears to be enolic. H. W.

Anthracene. VII. The Alkylation of Anthranol. Kurt H. Meyer and Hans Schlösser (*Annalen*, 1920, **420**, 126—133).—In continuation of previous work (A., 1911, i, 195), the authors have studied the alkylation of anthranol by alkyl sulphates and alkyl haloids respectively. The former shows the greater tendency towards the formation of O-ethers by direct exchange of the alkyl group for the metallic atom, whereas the latter cause alkylation in the nucleus to a much more pronounced extent. It is suggested that a part of the alkyl haloid is added at the active double bond of anthranol, yielding 9-alkylanthrone, which is transformed in the alkaline solution into 9-alkylanthranol; the latter can then react

further with alkyl haloid, one portion of it giving the O-ether, whilst another portion adds alkyl haloid and yields dialkylanthrone.

Anthranol methyl ether, $C_6H_4<\begin{matrix}C(OMe)\\CH\end{matrix}>C_6H_4$, coarse leaflets, m. p. 94°, is prepared by the action of methyl sulphate and alkali on an alcoholic solution of anthrone; when dissolved in boiling benzene and treated with phosphorus pentachloride, it yields 10-*chloroanthranol methyl ether*, yellow crystals, m. p. 154°, whilst with bromine in carbon disulphide solution it gives 10-*bromoanthranol methyl ether*, colourless crystals, m. p. 145°. When treated with aqueous potassium hydroxide and methyl iodide, anthrone is mainly converted into *methylanthranol methyl ether*, $C_6H_4<\begin{matrix}C(OMe)\\CMe\end{matrix}>C_6H_4$, m. p. 147°, together with very small quantities of dimethylanthrone, m. p. 95°, which, according to the older observations of Hallgarten, is the main product of the change. Methylanthranol methyl ether is transformed by bromine in carbon disulphide solution into ω-9-*dibromomethylanthrone*,

$$C_6H_4<\begin{matrix}CO\\CBr(CH_2Br)\end{matrix}>C_6H_4,$$

yellow crystals, m. p. 135—140° (decomp.) after darkening at 120°, the constitution of which is deduced from its formation from methyleneanthraquinone and bromine (following abstract).

With ethyl sulphate and alkali, anthrone gives *anthranol ethyl ether*, yellow plates, m. p. 73°, which yields a very unstable bromo-derivative, and is converted by amyl nitrite in acetic acid solution containing a little hydrochloric acid into anthraquinoneoxime. In agreement with Goldmann's data, anthranol is converted by ethyl iodide into diethylanthrone, m. p. 135°, and 9-ethylanthranol ethyl ether, m. p. 84°.

Anthrone is transformed by aqueous methylamine solution into N-*methyl*meso*anthramine*, $C_6H_4<\begin{matrix}C(NHMe)\\CH\end{matrix}>C_6H_4$, sulphur-yellow needles, m. p. 90° after softening at 85°; the *hydrochloride* forms *pale yellow crystals, m. p. 225°. The action of methyl iodide on* the base gives only unchanged material and anthraquinone, whilst the latter is obtained when methyl sulphate is used. H. W.

Anthracene. VIII. Methyleneanthraquinone. KURT H. MEYER (*Annalen*, 1920, **420**, 134—136).—Simple methylenequinones have been somewhat frequently described in the literature, but several of them have been shown by Pummerer and Cherbuliez (A., 1915, i, 419) to be dehydrophenols, whilst, more recently (A., 1919, i, 439), Pummerer has expressed the opinion that the remainder are more complex substances, which are probably also to be regarded as dehydrophenols. The author has now succeeded in isolating *methyleneanthraquinone*, $C_6H_4<\begin{matrix}CO\\C(:CH_2)\end{matrix}>C_6H_4$, by the condensation of a cold alkaline solution of anthranol with an excess of formaldehyde. It forms stable, pale yellow prisms, m. p. 148°, and

instantaneously adds bromine in carbon disulphide solution, yielding bromomethylbromoanthrone, m. p. 135—140° (decomp.) after becoming discoloured at 110°, identical with the product obtained by the bromination of methylanthranol methyl ether (preceding abstract). H. W.

Rotatory Dispersion of the Menthyl Esters of certain Keto-acids. H. Rupe and H. Kägi (*Annalen*, 1920, **420**, 33—84).—The present communication describes an extension of the work of Rupe and Lenzinger (A., 1913, i, 266, 884), who prepared a number of the esters, but only observed their specific rotations for the sodium *D*-line. The rotatory dispersions are now recorded. The following substances are described.

Menthyl cyanoacetate, m. p. 83·5°, $[\alpha]_{C}^{20}$ −64·15°, $[\alpha]_{D}^{20}$ −80·92°, $[\alpha]_{Hg}^{20}$ −95·21°, $[\alpha]_{F}^{20}$ −123·57° in benzene solution. Menthyl phenylpropiolate, m. p. 63—64°, $[\alpha]_{C}^{20}$ −57·31°, $[\alpha]_{D}^{20}$ −72·56°, $[\alpha]_{Hg}^{20}$ −85·9°, $[\alpha]_{F}^{20}$ −111·92° in benzene. Menthyl ethylacetoacetate, $[\alpha]_{C}^{20}$ −50·59°, $[\alpha]_{D}^{20}$ −63·85°, $[\alpha]_{Hg}^{20}$ −75·60°, $[\alpha]_{F}^{20}$ −98·39°. *Menthyl diethylacetoacetate*, b. p. 161°/9·5 mm., D_{4}^{20} 0·9638, $[\alpha]_{C}^{20}$ −44·35°, $[\alpha]_{D}^{20}$ −55·68°, $[\alpha]_{Hg}^{20}$ −65·53°, $[\alpha]_{F}^{20}$ −84·35° in substance, $[\alpha]_{C}^{20}$ −40·39°, $[\alpha]_{D}^{20}$ −50·77°, $[\alpha]_{Hg}^{20}$ −59·46°, $[\alpha]_{F}^{20}$ −76·50° in benzene. *Menthyl* iso*propylacetoacetate* (from menthyl sodioacetoacetate and *iso*propyl iodide in the presence of toluene at 120—125°), b. p. 158—159°/9 mm., D_{4}^{20} 0·9603, $[\alpha]_{C}^{20}$ −48·69°, $[\alpha]_{D}^{20}$ −61·53°, $[\alpha]_{Hg}^{20}$ −72·91°, $[\alpha]_{F}^{20}$ −95·05° in substance, $[\alpha]_{C}^{20}$ −47·32°, $[\alpha]_{D}^{20}$ −59·74°, $[\alpha]_{Hg}^{20}$ −70·58°, $[\alpha]_{F}^{20}$ −91·70° in benzene. *Ethyl diphenylmethylacetoacetate*, $CH_3\cdot CO\cdot CH(CHPh_2)\cdot CO_2Et$, small, shining rods, m. p. 89—90°. Menthyl diphenylmethylacetoacetate could not be obtained from menthol and the ethyl ester or from menthyl acetoacetate and diphenylbromomethane and alcoholic sodium ethoxide. Reaction could be caused to occur between menthyl sodioacetoacetate and diphenylbromomethane in the presence of dry benzene, giving a product which is resolved into diastereoisomerides by prolonged fractionation; l-*menthyl* d-*diphenylmethylacetoacetate* has m. p. 118°, $[\alpha]_{C}^{20}$ −33·83°, $[\alpha]_{D}^{20}$ −41·94°, $[\alpha]_{Hg}^{20}$ −48·18°, $[\alpha]_{F}^{20}$ −60·00°, whilst *l*-menthyl *l*-diphenylmethylacetoacetate has m. p. 90°, $[\alpha]_{C}^{20}$ −51·13°, $[\alpha]_{D}^{20}$ −65·15°, $[\alpha]_{Hg}^{20}$ −78·04°, $[\alpha]_{F}^{20}$ −103·94°, and l-*menthyl* dl-*diphenylmethylacetoacetate* has $[\alpha]_{C}^{20}$ −42·62°, $[\alpha]_{D}^{20}$ −53·69°, $[\alpha]_{Hg}^{20}$ −63·31°, $[\alpha]_{F}^{20}$ −82·43°. The rotatory dispersion curves of the diastereoisomerides differ widely from one another, and the *d*+*l*-form exhibits complex anomaly. Somewhat similar experiences are encountered with the benzylacetoacetic esters (compare Rupe and Lenzinger, *loc. cit.*); the most readily isolable ester is l-*menthyl* l-*benzylacetoacetate*, m. p. 68°, $[\alpha]_{C}^{20}$ −94·05°, $[\alpha]_{D}^{20}$ −121·21°, $[\alpha]_{Hg}^{20}$ −145·67°, $[\alpha]_{F}^{20}$ −196·73°, whilst l-*menthyl* dl-*benzylacetoacetate*, m. p. 48—51°, $[\alpha]_{C}^{20}$ −43·43°, $[\alpha]_{D}^{20}$ −55·10°, $[\alpha]_{Hg}^{20}$ −65·20°, $[\alpha]_{F}^{20}$ −85·85°, is also obtained; the *d*-ester could not be isolated in the pure condition. *l*-Menthyl benzylideneacetoacetate (from benzaldehyde and *l*-menthyl acetoacetate in the presence of hydrogen chloride, thus giving the ***hydrochloride***, needles, m. p. 118°, as intermediate product) has $[\alpha]_{C}^{20}$ −8·17°, $[\alpha]_{D}^{20}$ −10·97°, $[\alpha]_{Hg}^{20}$ −13·66°, $[\alpha]_{F}^{20}$ −21·27° in benzene solution. l-***Menthyl diacetylacetoacetate***, colourless, odourless oil, b. p. 172—173°/

11 mm., D_4^{20} 1·0239 (the pale blue *copper* salt was analysed), has $[\alpha]_C^{20}$ −61·49°, $[\alpha]_D^{20}$ −79·56°, $[\alpha]_{Hg}^{20}$ −96·34°, $[\alpha]_F^{20}$ −131·32° in substance, $[\alpha]_C^{20}$ −51·84°, $[\alpha]_D^{20}$ −66·88°, $[\alpha]_{Hg}^{20}$ −80·68°, $[\alpha]_F^{20}$ −110·64° in benzene solution. Attempts to prepare *l*-menthyl benzoylacetoacetate were unsuccessful. Menthyl benzoylacetate has $[\alpha]_C^{20}$ −50·95°, $[\alpha]_D^{20}$ −64·39°, $[\alpha]_{Hg}^{20}$ −76·15°, $[\alpha]_F^{20}$ −99·89° in benzene, whilst under similar conditions *l*-menthyl benzoylbenzylideneacetate has $[\alpha]_C^{20}$ −61·75°, $[\alpha]_D^{20}$ −78·62°, $[\alpha]_{Hg}^{20}$ −93·69°, $[\alpha]_F^{20}$ −123·84°. Menthyl *l*-benzoylcinnamylacetate, $CHPh{:}CH·CH_2·CHBz·CO_2·C_{10}H_{19}$ (Rupe and Lenzinger, *loc. cit.*), has $[\alpha]_C^{20}$ −67·41°, $[\alpha]_D^{20}$ −86·08°, $[\alpha]_{Hg}^{20}$ −102·18°, $[\alpha]_F^{20}$ −135·71°, but the diastereoisomeric ester could not on this occasion be isolated in a sufficiently pure condition for polarimetric investigation Menthyl *d*-benzoylphenylacetate has $[\alpha]_C^{20}$ +13·73°, $[\alpha]_D^{20}$ +21·10°, $[\alpha]_{Hg}^{20}$ +28·58°, $[\alpha]_F^{20}$ +49·91° in benzene, $[\alpha]_C^{20}$ −43·89°, $[\alpha]_D^{20}$ −58·91°, $[\alpha]_{Hg}^{20}$ −75·08°, $[\alpha]_F^{20}$ −93·57° in alcohol with one drop of piperidine. The dextrorotation is caused by the activity of the asymmetric complex of the acid preponderating over that of the menthol; in alcoholic solution, however, the ketonic rapidly passes into the enolic form, thus destroying the asymmetry of the carbon atom in the acid portion of the molecule and leaving an activity entirely due to the presence of the menthyl group. *Menthyl dibenzoylacetate*, colourless needles, m. p. 138·5—139°, has $[\alpha]_C^{20}$ −49·58°, $[\alpha]_D^{20}$ −64·07°, $[\alpha]_{Hg}^{20}$ −76·88°, $[\alpha]_F^{20}$ −104·18° in benzene.

The ethyl menthyl acetylsuccinates have also been investigated. The *a-ester*, $CO_2Et·CH_2·CHAc·CO_2·C_{10}H_{19}$, prepared from menthyl acetoacetate and ethyl chloroacetate in the presence of alcoholic sodium ethoxide, has b. p. 192—195°/9 mm., 111—112°/0·1 mm., D_4^{20} 1·0295, $[\alpha]_C^{20}$ −44·76°, $[\alpha]_D^{20}$ −56·67°, $[\alpha]_{Hg}^{20}$ −67·24°, $[\alpha]_F^{20}$ −87·97° in substance, $[\alpha]_C^{20}$ −45·59°, $[\alpha]_D^{20}$ −57·80°, $[\alpha]_{Hg}^{20}$ −67·99°, $[\alpha]_F^{20}$ −89·38° in benzene solution; the *β-ester*, $CO_2Et·CHAc·CH_2·CO_2·C_{10}H_{19}$, from menthyl chloroacetate and ethyl sodioacetoacetate, is a colourless, viscous oil, b.p. 200—202°/12 mm., 116—117°/*ca.* 0·1 mm., D_4^{20} 1·0267, $[\alpha]_C^{20}$ −38·77°, $[\alpha]_D^{20}$ −48·80°, $[\alpha]_{Hg}^{20}$ −57·45°, $[\alpha]_F^{20}$ −74·02° in substance, $[\alpha]_C^{20}$ −40·94°, $[\alpha]_D^{20}$ −51·59°, $[\alpha]_{Hg}^{20}$ −60·68°, $[\alpha]_F^{20}$ −78·29° in benzene. The product obtained by heating a mixture of menthol and ethyl acetylsuccinate is a mixture of 90% of the α- with 10% of the β-ester.

The enol content of several menthyl esters has been determined by Meyer's method of titration with bromine. The following percentages of enol are thus found, the figures for the corresponding ethyl esters being placed within brackets: menthyl acetoacetate, 17·37% (7·71%); menthyl ethylacetoacetate, 1·69% (3·1%); menthyl diacetylacetate, 72·72% (90%); menthyl acetylsuccinate, 0·65% (3·7%). Menthyl benzoylacetoacetate and menthyl benzoylphenylacetate do not unite with bromine.

On the basis of the present and previous communications, the authors are led to distinguish four types of abnormal rotatory dispersion: (i) total anomaly of a mixture of two substances with opposed activities (Tschugaev's extramolecular anomalous dispersion); (ii) total anomaly of a compound containing two different asymmetric complexes, one of which is dextro-, the other lævo-rotatory (Tschugaev's intramolecular anomalous dispersion); (iii) the

rotatory dispersion curve does not pass through a maximum or minimum, neither does it approximate to a horizontal line, but λ_a and λ_0^2 differ widely from the normal values and $\frac{1}{[a]}/\lambda^2$ gives bent or zig-zag lines (complex rotatory dispersion of Lowry and Dixon); (iv) apparently normal course of the curves and $\frac{1}{[a]}/\lambda^2$ gives straight lines, but λ_a and λ_0^2 differ greatly (at least $\pm 15\ \mu\mu$ for the former) from the normal value for the particular class of compound (relative anomaly).

The paper contains a criticism of the proposal by Lowry and Abram (T., 1919, **115**, 300) to delete the "relatively abnormal" classification: the author considers that sufficient substances are known, in which λ_a differs by 15—60 $\mu\mu$ and λ_0^2 by as much as five units from the normal figures for the class of substance without, however, exhibiting complex anomaly, to justify a separate classification. H. W.

The Alcohols of the Hydroaromatic and Terpene Series. III. *iso*Pulegol. Robert Howson Pickard, Harold Hunter, William Lewcock, and Hannah Smith de Pennington (T., 1920, **117**, 1248—1263).

1-Hydroxy-2-benzoylcamphor. A. L. W. E. van der Veen (*Zeitsch. Kryst. Min.*, 1920, **55**, 627).—Colourless, sharply developed crystals 1 cm. across were crystallised from a warm solution in light petroleum. D 1·242; m. p. 95°. The symmetry-class is rhombic-bisphenoidal, as shown by the distribution of the faces and by etching; $a:b:c = 0·6535:1·0247:1$. Optical data are given. Owing to the strong dispersion of the optic axes, brilliant colours are seen in parallel light between crossed nicols when viewed along an optic axis. L. J. S.

Essential Oil of Perylla nankinensis, Dene. Seiji Furukawa and Zenjirō Tomizawa (*J. Chem. Ind. Tokyo*, 1920, **23**, 342—363).—The formation, distribution, transformation, and chemical composition of the essential oil of *Perylla nankinensis*, Dene, were investigated. The oil and its parent substance (glucoside) are formed in the leaves only, but are later transported to the ear, and radiate from the sepals, the radiation being the most active during the flowering time. Both the oil and glucosides accumulate in the leaves gradually until the ears appear, and then remain constant until the beginning of the flowering time. With the appearance of the ears, the glucosides begin to decompose, finally disappearing after flowering. The oil distilled from the fresh plants at different stages of growth shows a gradual increase in aldehydes and decrease in ester until the end of the flowering time, whilst the oil from dried plants shows the reverse. The solubility of the oil decreases with the growth of the plants. To convert the glucosides into oil, the plants must be dried at low temperature to avoid decomposition of enzyme, which causes

resinification and decrease of solubility of the oil. The essential oils contain 20—30% of *l*-limonene, 44—57% of perillaldehyde, and a little *a*-pinene. The various derivatives of perillaldehyde were prepared and their properties studied. Perillaldehyde has b. p. 237°, D^{15} 0·9675, $[\alpha]_D^{20}$ −145·8°. The *a-anti*-aldoxime of the aldehyde, colourless crystals, has m. p. 102°, and is exceedingly sweet, being two thousand times as sweet as sugar and four to eight times as sweet as saccharin. The hydrochloride of the oxime, unstable, white crystals, has m. p. 114°. The *β-syn-aldoxime*, colourless, triclinic prisms, has m. p. 129°, and is not sweet. The phenylhydrazone, silky needles, and semicarbazone, colourless crystals, have m. p. 107·5° and 190—199° respectively. Perillonitrile, $C_9H_{13}\cdot CN$, has b. p. 123°/15 mm. and D^{19} 0·9488—0·9490, and is one-half as sweet as saccharin. Perillic acid, m. p. 132—133°, yields an amide, $C_9H_{13}\cdot CO\cdot NH_2$, colourless crystals, m. p. 164—165°. Perilla alcohol, b. p. 118—121°/11 mm., D 0·9690, forms an acetate, b. p. 123—124°/13 mm., D 0·9800.

CHEMICAL ABSTRACTS.

p-Cymene as a Solvent. A. S. WHEELER (*J. Amer. Chem Soc.*, 1920, **42**, 1842—1846).—Spruce turpentine consists largely of *p*-cymene, and for the isolation of the latter, air at the ordinary temperature is first drawn through the turpentine for ten hours, and then the turpentine is distilled with superheated steam in an apparatus arranged so that the vapours pass first through a 30% solution of sodium hydroxide and then into the condenser. The distillate is purified by shaking it with a 5% solution of sodium hydroxide, and then distilling it over sodium. So prepared, *p*-cymene has b. p. 176—176·5° and $n^{12\cdot5}$ 1·4905.

The solubilities of a whole series of organic compounds in this solvent have been determined, and are tabulated. Pure *p*-cymene containing a trace of *p*-anisidine only slowly turns yellow when exposed to light, whereas an impure specimen turns red. W. G.

The Acceleration of Vulcanisation. I. D. F. TWISS and S. A. BRAZIER (*J. Soc. Chem. Ind.*, 1920, **39**, 125—132T).—The temperature-coefficient for the vulcanisation process has approximately the same value for a mixture of rubber and sulphur as for a similar mixture containing aldehyde-ammonia as catalyst. The progress of the reaction is illustrated by curves representing the rate of attainment of a maximum tensile strength, the gradual decrease in extensibility, and the increase in the proportion of sulphur in combination with the rubber. Results are quoted of experiments using other substances as catalysts, and it is shown that *m*-phenylenediamine is less active than *p*-phenylenediamine.

D. F. T.

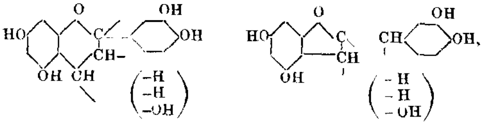
The Acceleration of Vulcanisation. II. A Discontinuity in the Effect of Vulcanisation. D. F. TWISS and C. W. H. HOWSON (*J. Soc. Chem. Ind.*, 1920, **39**, 287—289T).—The effect of 1% of "light" magnesium oxide in accelerating

vulcanisation is approximately equal to that of 0·5% of potassium hydroxide introduced as a solution in glycerol. Mercuric oxide also exerts a distinct catalytic effect. When 1% of hexamethylenetetramine is used as a catalyst in the presence of 1% of zinc oxide, the extensibility of the rubber does not decrease steadily, in the normal manner with progressive vulcanisation, but, after an initial decrease, suddenly begins to increase; after a brief period of this abnormal behaviour, a maximum is attained, and the rubber then resumes the normal decrease in extensibility. D. F. T.

Constitution of Catechin. II. MAXIMILIAN NIERENSTEIN (T., 1920, **117**, 1151—1156).

Tannins. V. Phloroglucinol Tannins and Catechins. Constitution of Gambier Catechu. KARL FREUDENBERG (*Ber.*, 1920, **53**, [*B*], 1416—1427).—The author classifies as *catechins* a number of substances which contain two benzene nuclei, one of which is phloroglucinol, whilst the other varies, but is commonly catechol. They are distinguished from the flavone dyes and anthocyanidins by a higher hydrogen content. They are colourless, form colourless lead salts, and do not unite with mineral acids. They are sparingly soluble in cold, freely in hot, water. They *give the pine-shaving reaction with phloroglucinol and yield* characteristic azobenzene derivatives. Their most characteristic property is their ability, in the presence of ferments or mineral acids in hot aqueous solution, or even when dried, both in presence and absence of atmospheric oxygen, to condense to amorphous tannins, the simpler members of which are colourless and soluble in water, whilst the more complex derivatives are insoluble and *more or less coloured. This classification includes, not only the* three ordinary catechins, but also substances such as cyanomaclurin, aromadendrin, colatin, cacaole, and others. When, now, the catechins are grouped together as phloroglucinol tannins, their behaviour is found to vary from member to member in precisely the same manner as that of the nearly related flavone dyes, anthocyanidins, and phenyl styryl ketones, so that the whole series appears *to be similarly constituted. It is therefore the more* remarkable that the only catechin which has been closely investigated should have had a formula assigned to it (von Kostanecki, A., 1907, i, 73, 334; 1908, i, 86) widely different from that of the natural dyes mentioned above, since it is considered to be derived from an ethyldiphenylmethane, whilst the latter are derivatives of $\alpha\gamma$-diphenylpropane. By the action of sodium and alcohol on *catechin tetramethyl ether, followed* by further methylation, von Kostanecki has obtained a pentamethyl ether which he considered to be 2 : 4 : 6-trimethoxy-3-ethylphenyl-3′ : 4′-dimethoxyphenylmethane, but which is now shown to be pentamethoxy-$\alpha\gamma$-diphenylpropane. Von Kostanecki's formula for Gambier catechu is therefore abandoned in favour of one of the alternative formulæ,

of which the author inclines to the latter, since the colour reactions of the tetramethyl ether resemble those of the coumarans.



The preparation of *veratraldehyde from protocatechualdehyde* is fully described, as is also that of phloroglucinol trimethyl ether (the latter is conveniently obtained by preliminary treatment of phloroglucinol with methyl alcohol and hydrogen chloride, followed by complete methylation with methyl sulphate or by the action of heat on trimethylcarbonatophloroglucinol, b. p. 195—200°/ Volmer pump vacuum). The phloroglucinol ether is converted into trimethylphloroacetophenone, which condenses with veratraldehyde to 2:4:6-trimethoxyphenyl 3′:4′-dimethoxystyryl ketone (compare Tutin and Caton, T., 1910, **97**, 2062). On reduction with hydrogen in the presence of platinum, the unsaturated ketone is reduced to 2:4:6:3′:4′-pentamethoxy-αγ-diphenylpropane, colourless, rectangular crystals, m. p. 87—88°, which is identical in all respects with the ether obtained from Gambier catechu by Kostanecki and Lampe (*loc. cit.*), for which, however, these authors found a somewhat lower melting point (compare Nierenstein, T., 1920, **117**, 971, 1151). H. W.

Lignin. III. Preparation of a Tannic Acid from the Lignosulphonic Acids. MAX HÖNIG and WALTER FUCHS (*Monatsh.*, 1920, **41**, 215—222. Compare this vol., i, 291).—When aqueous solutions of the barium salts of the three fractions of the *lignosulphonic acids* are boiled with saturated barium hydroxide solution, they yield insoluble precipitates and readily soluble substances. The former differ from one another, and their composition has not yet been elucidated; they are all readily oxidised by alkaline permanganate, but the only product which could be characterised definitely was oxalic acid, obtained from the first fraction. The soluble *substances*, on the other hand, appear to be identical with one another, and the analytical results are in agreement with the formula $C_{18}H_{30}O_{10}SBa$, so that they are probably derived from an acid, $OMe{\cdot}C_{16}H_{27}O_4(SO_3H){\cdot}CO_2H$. The aqueous solution of the salt gives greenish-grey, green, and white precipitates with iron chloride, copper chloride, and lead acetate respectively, and voluminous precipitates with quinine hydrochloride and gelatin; it is almost quantitatively precipitated by formaldehyde and hydrochloric acid. About 70% of it is absorbed

from acid solution by hide powder. The substance therefore has all the properties of a tannic acid of the catechu group, with such modifications as are caused by the sulphur content; when fused with potassium hydroxide, it gives protocatechuic acid in good yield. H. W.

Thionaphthen in Coal Tar. R. WEISSGERBER and O. KRUBER (*Ber.*, 1920, **53**, [*B*], 1551—1565).—The presence of thionaphthen in coal tar has frequently been suspected, particularly since its investigation by Gattermann and Lockhardt (A., 1894, i, 92), and subsequently by Bezdrik, Friedländer, and Koeniger (A., 1908, i, 200), has shown that it is extraordinarily like naphthalene, but up to the present all the efforts which have been made to identify it have been unsuccessful. This, however, has now been accomplished in the following manner, the method adopted being in the first instance similar to that used by V. Meyer for the isolation of thiophen. Crude naphthalene is sulphonated with a greatly deficient amount of sulphuric acid at 90—100°, and the sulphonated product is decomposed with steam in the presence of a little sulphuric acid at 145°. The product has m. p. about 73° and contains 2—3% of sulphur. Repetition of the process gives a material containing about 5—6% of sulphur, which can be increased to 12—14% by freezing out the naphthalene. The product obtained in this manner is dissolved in glacial acetic acid and treated with hydrogen peroxide, when thionaphthen-S-dioxide, long needles, m. p. 142°, is obtained, which is identical in all respects with the synthetic product. The actual isolation of thionaphthen from "enriched" naphthalene has been effected by the use of Friedländer's mercuric acetate method (*loc. cit.*), but it is essential to guard against undue rise in temperature during the action, which can be readily effected by working with methylalcoholic solutions. By a similar process of partial sulphonation, followed by use of mercuric acetate, it has been found possible to isolate thionaphthen from technical "pure" naphthalene (containing 0·3—0·4% S), about 2 grams of the substance being obtained from 80 kilos. of naphthalene.

The industrial preparation of thionaphthen from crude naphthalene has also been investigated. It is found that thionaphthen is converted by sodium at 100—120° into a yellowish-brown *sodium compound*, which can readily be freed from adherent impurities by washing with benzene, and which decomposes, with re-formation of thionaphthen, when treated with ice-cold water; the yields, however, leave much to be desired, and the heating requires to be very carefully regulated. Far better results are obtained when sodamide is used (in the proportion of two molecules to one molecule of thionaphthen); reaction is complete at 120°, and practically the whole of the thionaphthen is liberated by water, the simultaneous formation of sodium sulphide appearing to be avoided. The process is applicable to "enriched"

naphthalene, and it is further found that the pre-formed sodamide may with advantage be replaced by sodium and dry ammonia.

The constitution of the sodium compound is discussed, but a definite conclusion is not reached. The possible desmotropic forms all contain a reactive methylene group, the presence of which cannot be established by the usual reagents, such as aromatic aldehydes, nitrous acid, or ethyl oxalate, which are indifferent towards thionaphthen. Under special conditions, however, the latter reacts with magnesium ethyl bromide, giving a compound, which is decomposed by carbon dioxide into thionaphthen-2-carboxylic acid, m. p. 236° (see later). At least one hydrogen atom must therefore be regarded as labile, and it must be assumed that the presence of the sulphur atom thus influences the neighbouring hydrogen atom, since substitution occurs preferably, and sometimes exclusively, in this position.

The action of carbon dioxide on sodium thionaphthen suspended in an indifferent solvent, such as toluene, gives rise to a mixture of the sodium salts of thionaphthen-2-carboxylic and -2:3-dicarboxylic acids, which can be separated by taking advantage of the widely differing acidities or by fractionation of their esters. The latter acid has been described previously, and the former is orientated by converting it through its azide into the well-known *a*-hydroxythionaphthen. It appears that the product obtained by fusion with sodamide consists of about two-thirds monosodium- and one-third disodium-thionaphthen.

The following individual compounds are described: *methyl thionaphthen-2-carboxylate*, coarse prisms, m. p. 72—73°, b. p. 171°/14 mm.; *ethyl thionaphthen-2-carboxylate*, indistinct crystals, m. p. 36—37°, b. p. 181—183°/vacuum; *thionaphthen-2-carboxylic acid*, colourless, slender needles, m. p. 236° (*chloride*, colourless leaflets, m. p. 88—89°, b. p. 173—175°/19 mm.; *amide*, slender needles or leaflets, m. p. 177°; *hydrazide*, colourless, shining leaflets, m. p. 184—185°; *azide*, long, colourless needles, m. p. 108° [decomp.]); *urethane* of 2-*aminothionaphthen*, yellow crystals, m. p. 161°; 2-hydroxythionaphthen, m. p. 34—35° (the acid is not identical with that prepared by Friedländer and Link from *o*-mercaptobenzaldehyde and chloroacetic acid, which has m. p. 114°, and is designated thionaphthen-2-carboxylic acid by these authors); *methyl thionaphthen-2:3-dicarboxylate*, long, colourless prisms, m. p. 91°, b. p. 213—215°/18 mm.; thionaphthen-2:3-dicarboxylic acid, m. p. 250—251°; *thionaphthen-2:3-dicarboxylic anhydride*, pale yellow needles, m. p. 171°; *thionaphthen-2-carboxyamido-3-carboxylic acid*, $C_6H_4<\overset{C(CO_2H)}{\underset{S}{\text{——}}}>C{\cdot}CO{\cdot}NH_2$, short, colourless needles, m. p. 221° (decomp.), and *thionaphthen-3-carboxyamido-2-carboxylic acid*, $C_6H_4<\overset{C(CO{\cdot}NH_2)}{\underset{S}{\text{——}}}>C{\cdot}CO_2H$, short needles grouped in rosettes, m. p. 193° (decomp.), are obtained by the action of methyl-alcoholic ammonia on the

anhydride, and are separated by fractional crystallisation from glacial acetic acid. Their constitution is deduced by degrading them by Hofmann's method to the corresponding amino-acids, and warming the latter with dilute sulphuric acid, whereby they are converted into 2-hydroxythionaphthen, m. p. 34—35°, and 3-hydroxythionaphthen, m. p. 70°, respectively. *Thionaphthen-2:3-dicarboxylimide*, golden-yellow leaflets, m. p. 236—237°, is prepared by heating either of the acid amides at 200—220° until evolution of water vapour ceases, or. less advantageously, by heating the anhydride in a current of ammonia or by melting the anhydride with the calculated amount of carbamide. Degradation of the imide by Hofmann's method yields exclusively 3-hydroxythionaphthen, so that thionaphthen can readily be converted into thioindigo-red through thionaphthen-2:3-dicarboxylic acid.

H. W.

Additive Compound of Cinchonine and Cacodyl Chloride. L. C. Maillard and E. Murlay (*Bull. Soc. chim.*, 1920, [iv], **27**, 756—769).—Cacodyl chloride combines directly or in chloroform solution with cinchonine to give a *compound*, $C_{19}H_{22}ON_2,Me_2AsCl$, and the crystals obtained from chloroform solution contain two molecules of the solvent. This compound is immediately decomposed by water, and cacodyl oxide is obtained. If the compound is decomposed by commercial ether, the anhydrous basic hydrochloride of cinchonine, $C_{19}H_{22}ON_2,HCl$, is obtained in a crystalline form. In the additive compound described above, the chlorine may be estimated directly by addition of nitric acid and silver nitrate.

W. G.

Proteinogenous Amines. VI. The Preparation of Histidine from Blood Corpuscle Paste. Milton T. Hanke and Karl K. Koessler (*J. Biol. Chem.*, 1920, **43**, 521—526).—The authors describe in full detail a process for the preparation of histidine from blood corpuscle paste; an average yield of 15 grams of pure histidine dichloride is obtained from 500 c.c. of the paste.

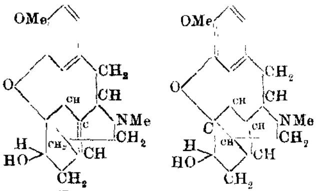
J. C. D.

Preparation of Compounds of the Morphine Alkaloids with a Derivative of Barbituric Acid. Society of Chemical Industry in Basle (D.R.-P. 322335; from *Chem. Zentr.*, 1920, iv, 392).—The alkaloids of the morphine group or their derivatives, either in the free state or as salts, are allowed to react with diallylbarbituric acid in the presence of a suitable solvent or diluent if required. The following compounds are described: *morphine–diallylbarbituric acid*, needles, m. p. 258°; *diacetylmorphine–diallylbarbituric acid*, colourless crystals, m. p. 186°; *ethylmorphine–diallylbarbituric acid*, crystalline mass; *allylmorphine sulphate*, m. p. 171°; *allylmorphine–diallylbarbituric acid*; *codeine–diallylbarbituric acid*, m. p. 105°; *dihydromorphine–*

diallylbarbituric acid, m. p. 125°; *dihydrocodeine-diallylbarbituric acid*, m. p. 95°.

H. W.

Codeine. Martin Freund, W. W. Melber, and Erich Schlesinger (*J. pr. Chem.*, 1920, [ii], **101**, 1—37).—During recent years, doubts have been cast on the validity of the formula (I) proposed for codeine by Knorr and his co-workers, by Gadamer and von Braun (A., 1914, i, 1138), and the alternative formula (*II*) has been put forward by Freund (*compare* Freund and Speyer A., 1916, i, 738).



(I.) (II.)

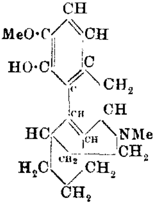
A series of attempts to gain further insight into the problem is now described; those starting from dihydrocodeine or chlorodihydrocodide did not furnish the desired information, but better results were obtained with deoxycodeine (Knorr and Waentig, A., 1917, i, 957) as initial material. This substance is reduced by sodium and alcohol to a compound, which has been described by the latter authors as dihydrodeoxycodeine, but which is now shown to be a tetrahydro-derivative; when, however, it is acted on by palladium and hydrogen, an isomeric tetrahydro-derivative is produced, the formation of which cannot be accounted for on the basis of Knorr's formula, but which is readily explained by the authors' modification thereof.

Dihydrocodeine, m. p. 86—88° (Oldenburg, D.R.-P. 260233, gives 62—63°), is unaffected by treatment with sulphuric and chromic acids under varied conditions, but is transformed by concentrated nitric acid in glacial acetic acid solution into *nitrodihydrocodeine*, yellow, crystalline powder, m. p. 221°. *Dihydrocodeine methiodide*, m. p. 257°, is readily obtained from its components, and is converted by dilute potassium hydroxide solution into *de*-N-*methyldihydrocodeine*, which could not be caused to crystallise, but which was readily converted into *de*-N-*methyldihydrocodeine methiodide*, colourless leaflets (+$\frac{1}{3}H_2O$), m. p. 173—176° (decomp.) after softening at 170° (the *perchlorate* of the base has m. p. 201—202°). *Dihydrode*-N-*methyldihydrocodeine* is obtained as a pale yellow, non-crystallisable syrup by the reduction of de-*N*-methyldihydrocodeine by hydrogen in the presence of palladium, and yields a *methiodide*, yellow powder, m. p. 219—221°, from alcohol or glacial acetic acid, colourless rods, m. p. 221—224°, from water. The methiodides evolve trimethylamine abundantly when treated with concentrated alkali hydroxide,

but the corresponding nitrogen-free bases are too readily decomposed to permit their isolation.

In the hope of obtaining better results with an analogous substance in which the hydroxyl group is not present, dihydrocodeine has been converted by phosphorus pentachloride in chloroform solution into *chlorodihydrocodide*, plates, m. p. 172—174°, which is transformed by hydrogen peroxide into *chlorodihydrocodide amino-oxide*, colourless leaflets (+ $3H_2O$), m. p. 214° (decomp.), which yields the original material on treatment with sulphurous acid, and by nitric acid in hot glacial acetic acid solution is converted into a *substance*, $C_{17}H_{24}O_5N_2Cl$ [?], pale yellow, crystalline powder, m. p. 223—224°, the constitution of which was not further elucidated. *Chlorodihydrocodide methiodide*, small, colourless, matted needles, m. p. 244° (decomp.), is prepared from its components, and is converted by potassium hydroxide into *de-N-methylchlorodihydrocodide*, m. p. 103° after previous softening, which combines with methyl iodide to give *de-N-methylchlorodihydrocodide methiodide*, colourless needles, m. p. 272°; the corresponding nitrogen-free base was too unstable to permit its isolation. De-*N*-methylchlorodihydrocodide is reduced by hydrogen in the presence of palladium to *dihydrode-N-methylchlorodihydrocodide*, which could not be caused to crystallise, but which readily yields *dihydrode - N - methylchlorodihydrocodide methiodide*, colourless, slender needles decomposing at 290—291°; the latter is decomposed by boiling alkali, with evolution of trimethylamine and simultaneous decomposition of the nitrogen-free substance.

α-Chlorocodide is reduced by hydrogen in the presence of colloidal palladium to *α-dihydrodeoxycodeine*, which could not be caused to crystallise; it yields an oily *hydriodide*, *methiodide* and *perchlorate*, and a solid, but amorphous, *picrate*, *aurichloride*, and *platinichloride*.

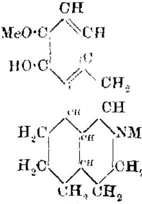


(III.)

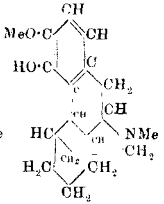
Dihydrodeoxycodeine (III), coarse, crystalline plates (+ $0{\cdot}5H_2O$), m. p. 117—119°, $[\alpha]_D^{18}$ + 88·71° in alcoholic solution (*hydriodide*, pale brown needles, m. p. 245°), is prepared by the electrolytic reduction of chlorodihydrocodide at a lead cathode, or in a similar manner from α- or β-chlorocodide or from deoxycodeine; the base obtained from β-chlorocodide, however, had m. p. about 126—130° after previous softening. The phenolic character of the base derived from deoxycodeine is particularly established by the isolation of the *methiodide* of the *methylated base*, long, flat needles, m. p. 245°. It would appear that deoxycodeine is not formed, as Knorr and Waentig (*loc. cit.*) suggest, by simple replacement of the hydroxyl group by hydrogen, but that it is formed by fission of the oxygen bridge.

Deoxycodeine hydrochloride is obtained by a modification of the

method of Knorr and Waentig (*loc. cit.*), and is reduced by hydrogen in aqueous solution in the presence of palladium to *β-tetrahydrodeoxycodeine* (IV); the base crystallises from methyl or ethyl alcohol in six-sided leaflets (+1 molecule of solvent), m. p. 147—148°; it is feebly lævorotatory in alcoholic solution. The *hydrochloride*, m. p. about 262° (+1EtOH), the *hydriodide*, long needles ($+H_2O$), m. p. 240—241°, and the *methiodide*, m. p. 263°, are described. All attempts to hydrogenate the base further were unsuccessful. The *N*-methyl group could not be removed by means of cyanogen bromide. The presence of the hydroxyl group could not be established by the help of acetic anhydride, benzoyl chloride, or chloroacetyl chloride, but the base is converted by methyl sulphate and sodium hydroxide into *methoxytetrahydrodeoxycodeine*, which was identified as the *methiodide*, prisms, m. p. 255—256° after previous softening; the latter is converted by very concentrated potassium hydroxide solution into *de-N-methylmethoxytetrahydrodeoxycodeine*, pale yellow oil, which yields a *hydriodide*, small rods, m. p. about 185° after softening from 175°, and a *methiodide*, prismatic rods, m. p. 188° after softening at 185°. The action of concentrated potassium hydroxide solution on the methiodide leads to the copious evolution of trimethylamine and the formation of small quantities of a pale yellow oil, which could not be caused to crystallise. *Bromotetrahydrodeoxycodeine*,



(IV.)



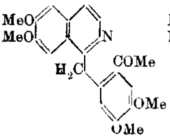
(V.)

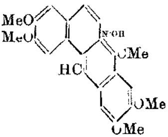
$$C_{18}H_{24}O_2NBr,EtOH,$$

needles, m. p. about 135° (decomp.) after softening from 120°, is prepared by the interaction of bromine and the β-base in chloroform solution; the *hydrochloride*, *hydrobromide*, and *hydriodide* are viscous salts, which could not be caused to crystallise. When subjected to electrolytic reduction, the bromo-compound regenerates the parent substance. α-Tetrahydrodeoxycodeine (formula V), small leaflets or rods, m. p. 132°, is prepared by the reduction of dihydrodeoxycodeine, m. p. 117—119°, by hydrogen and palladium, or by electrolytic reduction of α-dihydrodeoxycodeine. The identity of this substance with the "deoxydihydrocodeine" obtained by Knorr and Waentig by the action of sodium and alcohol on deoxycodeine is established by its melting point and that of its hydrochloride [155° (decomp.)], and also by its conversion into α-methoxytetrahydrodeoxycodeine methiodide, m. p. 247° (Knorr and Waentig give m. p. 248—249°).

H. W.

Acetylpapaverine and Coralyne [Hexadehydrocoralydine]. WILHELM SCHNEIDER and KURT SCHROETER (*Ber.*, 1920, **53**, [*B*] 1459—1469).—Papaverine is converted by acetic anhydride, which has been previously warmed to 85° with a little concentrated sulphuric acid, into a yellow, crystalline salt, $C_{24}H_{25}O_9NS,H_2O$. The corresponding quaternary ammonium base passes in warm aqueous solution into an isomeric ketonic base, from which the original salts are regenerated by addition of acid. The phenomena are thus very similar to those observed with berberine, and, more particularly, with dehydrocorydaline (Haars, A., 1905, i, 462) from which the present compound differs in containing two atoms of hydrogen less in the molecule. The constitution of the substance is further elucidated by its conversion into *m*-hemipinic acid; it behaves in this respect in the same manner as coralydine (Pictet, A., 1913, i, 1224; 1916, i, 418), and for this reason the authors propose the name coralyne. It therefore appears that the primary product of the action of sulphoacetic anhydride on papaverine is acetylpapaverine (I), which passes by ring closure into the sulphoacetate of the isomeric quaternary coralyne base (II).


(I.)


(II.)

Coralynesulphoacetate, $C_{22}H_{22}O_4N\cdot SO_3\cdot CH_2\cdot CO_2H,H_2O$, forms intensely yellow needles, m. p. 277° (decomp.), which fluoresce strongly in aqueous solution. The following salts are readily prepared from it: *chloride*, $C_{22}H_{22}O_4NCl,2\cdot 5H_2O$, slender, yellow needles; *iodide*, $+H_2O$, golden-yellow needles, m. p. 278° (decomp.); *hydrogen sulphate*, $+2\cdot 5H_2O$, voluminous, pale yellow precipitate; *nitrate*, $+H_2O$, small, yellow needles, which decompose above 270° without appearing to melt.

Acetylpapaverine (*ψ-coralyne*), yellowish-grey crystals, m. p. 140—141°, is readily obtained by heating a solution of coraly sulphoacetate in water with an excess of sodium hydroxide until the solution, which originally has a dark colour, owing to the presence of the ammonium hydroxide form of coralyne, becomes pale orange; the ψ-base is stable in the dry state or when dissolved in benzene, but on contact with water or alcoholic solutions is more or less rapidly converted into the ammonium form the rate being generally such as can be readily followed by titration with *N*/10-acid. It is interesting to note that this change is accompanied by the development of fluorescence in the solution *Acetylpapaverineoxime* has m. p. 207°, whilst the *phenylhydrazone* forms colourless, matted needles, m. p. 208°. When treated with methyl iodide in benzene solution at 100°, acetylpapaverine gives the corresponding *methiodide*, small, pale yellow needles

m. p. 219—220°, but in methyl-alcoholic solution it yields the quaternary coralyne iodide. H. W.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXXIV. Affinity Constants and Esterification of the Pyridinecarboxylic Acids. RUDOLF WEGSCHEIDER (*Monatsh.*, 1920, **41**, 185—198).—It has been shown (this vol., i, 740) that the formation of hydrogen esters of aminodicarboxylic acids takes place, generally, in a fairly regular manner, except in the instance of the semi-hydrolysis of the normal esters, and attempts are now made to secure a more uniform conception of the esterification of the pyridinecarboxylic acids than has previously been possible. It is found that the apparently irregular affinity constants of the pyridinecarboxylic acids can be brought into line with the Ostwald factor rule in the same manner as the aromatic acids if it is assumed that these constants are influenced by internal salt formation. In general, the same factors can be used for the substituents as in the case of the aromatic acids, except for the methyl group, for which larger factors must be chosen. The formation of hydrogen esters of the pyridinecarboxylic acids in general follows the same rules as are usually valid if a steric influence is not ascribed to the nitrogen atom of the ring, and the strength of the carboxyl group is regarded as determined by a suitably modified factor rule. Exceptions are only encountered in the case of semi-hydrolysis, and this is by no means unusual. H. W.

Manufacture of the Allyl Ester of 2-Phenylquinoline-4-carboxylic Acid. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat., 150401).—Like the alkyl esters, the allyl ester of 2-phenylquinoline-4-carboxylic acid is tasteless, and has the further advantage of dissolving uric acid more readily than either the alkyl esters or the acid itself. It may be prepared by any of the usual methods of esterification, such as the action of an allyl haloid on a salt of the acid or by the action of allyl alcohol on the acid chloride, or on the acid itself in presence of hydrogen chloride or sulphuric acid. The ester boils at 260°/15 mm., and melts at 30°. Its hydrochloride crystallises from alcohol in small, citron-yellow needles, m. p. 145—147°, which are immediately decomposed by water. G. F. M.

Quinuclidines. JAKOB MEISENHEIMER (*Annalen*, 1920, **420**, 190—239).—The term quinuclidines has been ascribed by Koenigs (A., 1905, i, 824) to a series of bases derived from piperidine by joining the nitrogen atom to the para-carbon atom by a bridge of two carbon atoms, and the isolation of 3-ethylquinuclidine has been described. The present communication deals with the preparation of quinuclidine itself and of benzoquinuclidine according to the general method of Koenigs. The former substance has been described previously by Löffler and Stietzel (A., 1909, i, 181), but

their data differ so widely from those of the present author that it is impossible for them to have been dealing with the pure compounds. (In the following, their data are recorded in brackets after the individual substances.)

[With JULIUS NERESHEIMER and WILHELM SCHNEIDER.]—4-Pyridylethanol, colourless, viscous syrup, b. p. 151—152°/13—14 mm. (125—126°/15 mm.), is prepared by the action of formaldehyde on 4-methylpyridine, obtained by fractionation of commercial 3-methylpyridine [the method of purification by means of mercuric chloride recommended by Ahrens (A., 1905, i, 232) does not appear to be effective]; the yield is only very small, owing to the simultaneous production of di- and tri-methylol. The corresponding picrate has m. p. 134—135° (122—123°). The alcohol is converted by fuming hydriodic acid and red phosphorus into *4-pyridylethyl iodide hydriodide*, m. p. 186—187° after darkening at about 180°, from which the corresponding picrate, slender, pale yellow needles, m. p. 114—115° (108—110°), is obtained; the latter readily decomposes in boiling aqueous or alcoholic solution, with the formation of 4-vinylpyridine picrate (see later). 4-Pyridylethyl iodide is a colourless oil, which readily decomposes spontaneously into a polymeric iodide, m. p. 267—268° (decomp.) after softening at 260° (216—218°). *4-Pyridylethyl chloride hydrochloride*, m. p. above 260° (decomp.), is prepared from 4-pyridylethanol and fuming hydrochloric acid; the corresponding *picrate* crystallises in slender, yellow needles, m. p. 130—131°, whilst the platinichloride has m. p. 207° (decomp.) (147—148°). The free base is a colourless oil, which readily loses hydrogen chloride and forms 4-vinylpyridine in the presence of alkali hydroxide; it is transformed when gently warmed into a *polymeric quinuclidine chloride*, m. p. 255—260° (decomp.).

4-*Vinylpyridine*, almost colourless oil, b. p. 59°/12 mm. (slight decomp.), is best obtained by the action of boiling methyl-alcoholic potassium hydroxide solution on 4-pyridylethyl iodide hydriodide [the *picrate*, yellow, shining leaflets, m. p. 198—199° (decomp.) after previous softening when slowly heated, and the *platinichloride*, which softens at about 200°, but does not melt below 350°, are described]. Potassium permanganate oxidises it to a mixture of formic and *iso*nicotinic acids.

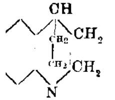
4-Piperidylethanol, almost colourless, viscous liquid, b. p. 140—141°/12—14 mm. (120—125°/15 mm.), is prepared by the reduction of 4-pyridylethanol by sodium and ethyl alcohol, and is converted by fuming hydriodic acid and red phosphorus into 4-piperidylethyl iodide hydriodide, colourless needles, m. p. 190—191° after darkening at 186° (158—159°). The latter is transformed by a slight excess of sodium hydroxide in warm aqueous solution into quinuclidine, which is conveniently isolated as the picrate, m. p. 275—276° (decomp.) after previous softening (213—215°); the free base has m. p. 158° after softening at 154° in a sealed capillary tube, and is very volatile for a substance of such high melting point. It is remarkably stable, and is scarcely

affected by concentrated sulphuric acid or nitric acid at 100°, or by potassium permanganate in sulphuric acid solution. The *platinichloride*, m. p. 238—240° (decomp.), and the *aurichloride*, large, shining leaflets, m. p. 271—273° (decomp.) after previous softening, are described. Quinuclidine unites with ethyl iodide to give the corresponding *ethiodide*, thin plates, m. p. 270—271° (slight decomp.), from which the platinichloride, leaflets, m. p. 271—272° after previous darkening (212°), is obtained.

[With OSCAR FINN and WILHELM SCHNEIDER.]—Lepidine, when heated on the boiling-water bath with 20% formaldehyde solution, yields a mixture of 4-quinolylpropanediol (picrate, m. p. 170°) and 4-quinolylethanol, prisms, m. p. 63° (picrate, m. p. 155—157°) (compare Koenigs, *loc. cit.*). The ethanol is somewhat unstable towards hydrochloric acid, which, at 100°, converts it into the *dimolecular 4-vinylquinoline* (see later). It is converted by hydriodic acid (D 1·96) and red phosphorus at 95° into *4-quinolylethyl iodide hydriodide*, yellow, six-sided plates, m. p. 173°; the salt is stable towards light and air when pure, but loses hydrogen iodide when its aqueous or alcoholic solution is boiled, and forms dimolecular 4-vinylquinoline. *4-Quinolylethyl iodide picrate* forms long needles, m. p. 154°. The corresponding free *base* is less stable than its salts, and loses hydrogen iodide in aqueous solution, with the formation of 4-vinylquinoline and other products. The *readiest method of preparing 4-vinylquinoline consists in boiling* a solution of 4-quinolylethyl iodide hydriodide in aqueous acetone with aqueous sodium hydroxide solution; the free base is purified through the *picrate*, slender needles, m. p. 188—189°, and is thus obtained as a pale brown, viscous oil, which gradually solidifies when preserved in a desiccator, and cannot be distilled even under greatly diminished pressure, owing to the readiness with which it polymerises. It is oxidised by potassium permanganate in sulphuric acid solution to formic and 4-quinolinecarboxylic acids. The *platinichloride*, broad needles, m. p. above 275°, is described. *Bimolecular 4-vinylquinoline*, coarse crystals, m. p. 148—149°, is obtained in the pure state by evaporation of a solution of the unimolecular variety in aqueous hydrochloric acid and cautious liberation of the base by addition of alkali in the presence of ether. It is neutral towards litmus, non-volatile with steam, and cannot be distilled; it does not decolorise acid permanganate. The *hydrochloride*, m. p. between 280° and 290°, the *platinichloride*, which does not melt below 340°, and the *picrate*, thin, yellow needles, m. p. 242—243° (decomp.) after previous softening and darkening, are described. 4-Vinylquinoline picrate is transformed by boiling absolute alcohol into *4-quinolylethyl ethyl ether picrate*, broad, shining needles, m. p. 171—172° (decomp.) after marked softening at 140° when slowly heated, m. p. 140—145°, followed by resolidification and re-melting at 171—172°, when rapidly heated, the variations being due to the elimination of ethyl alcohol and formation of 4-vinylquinoline picrate, which then undergoes partial decomposition; a similar change appears to be caused by

boiling methyl alcohol, the *picrate* so obtained having m. p. 167—168° (decomp.). 4-*Quinolylethyl ethyl ether* is an almost colourless liquid, b. p. 169—170°/11—12 mm. [*platinichloride*, flat, golden-yellow prisms, m. p. 183—184° (decomp.) when rapidly heated].

Tetrahydro-4-quinolylethanol, pale yellowish-green, viscous liquid, b. p. 196—198°/11—12 mm., is prepared by the reduction of 4-quinolylethanol by sodium and ethyl alcohol; it does not yield a crystalline picrate or platinichloride, and reduces gold chloride to metallic gold. On treatment with red phosphorus and fuming hydriodic acid, the ethanol gives *tetrahydro-4-quinolylethyl iodide hydriodide* (m. p. about 100—105° in the crude condition), which is converted by aqueous sodium hydroxide solution at 60—70° into *benzoquinuclidine* (annexed formula), shining leaflets, m. p. 68—69° (*platinichloride*, yellowish-red prisms, which soften at 225° and decompose at 230°; *picrate*, slender needles, m. p. 195—196°). *Benzoquinuclidine ethiodide* forms long needles, m. p. 217—218°, and is converted by moist silver oxide into the corresponding quaternary base. H. W.



Alkylation of Pyrazolones by means of Sodium Alkyloxides. LUDWIG WOLFF and ERNST THIELEPAPE (*Annalen*, 1920, **420**, 275—284).—Wolff's method for the replacement of the oxygen atom of ketones and aldehydes by hydrogen which depends on the action of sodium ethoxide on the corresponding hydrazones (A., 1912, i, 988) gives partly abnormal results when applied to pyrazolones, since alkylation is found to occur.

When 3-methylpyrazolone is heated with methyl-alcoholic sodium methoxide for fifteen hours at 220° and subsequently for nine hours at 250° it yields a mixture of butyric acid (41%) and 3:4-dimethylpyrazolone (39%), colourless crystals, m. p. 267—268°, the identity of which is established by comparison with a specimen prepared from ethyl methylacetoacetate and hydrazine hydrate; with sodium ethoxide, 3-methyl-4-ethylpyrazolone, m. p. 229°, is mainly produced, butyric acid being formed in minor quantity, whilst, with sodium propoxide, 3-methyl-4-propylpyrazolone, m. p. 206—207°, is obtained. The success of the experiment is largely dependent on the use of absolutely anhydrous alcohol, since under similar conditions, but with Kahlbaum's propyl alcohol which had not been specially treated, pyrazolylpyrazolone, m. p. 259°, was isolated in good yield. 3:4-Dimethylpyrazolone was not affected by being heated with sodium ethoxide solution during twenty-two hours at 250°. Phenylmethylpyrazolone is transformed by sodium ethoxide at 170—190° into a mixture of bisphenylmethylpyrazolone, which does not melt below 300°, and bisphenylmethylethylpyrazolone, m. p. 149—150°; more complete ethylation is effected at 220°. 3:5-Dimethylpyrazole is converted by sodium ethoxide at 250°

into a *substance*, $C_{12}H_{20}N_4$, m. p. 253° [*picrate*, m. p. 224—226° (decomp.)], which is probably *tetramethylethylpyrazolylpyrazole*.

H. W.

New Cases of Isomerism in the Isatin Series. IV. GUSTAV HELLER (*Ber.*, 1920, **53**, [*B*], 1545—1551. Compare A., 1917, i, 219).—Further experiments have shown that isatol has about three times the molecular weight calculated for the simple formula when dissolved in boiling glacial acetic acid or in freezing phenol or veratrole; the phenomenon is considered to be due to association rather than to polymerisation. The conversion of isatol into isatin is not a simple rearrangement, but appears to occur with intermediate formation of bimolecular isatoid-like substances. The typical properties of the isatols appear to be more clearly exhibited by dimethylisatol (the dimethylisatin, III, of A., 1918, i, 235), which is not immediately affected by alkali and is unimolecular as shown by the smooth conversion of its methyl ether into the unimolecular lactim ether when heated with glacial acetic acid; its ready conversion into a basic substance, insoluble in alkali, appears to differentiate it from methylisatoid.

The formula previously proposed for isatinone (A., 1919, i, 282) is now abandoned, since the substance is found to be identical with methylisatoid prepared by Baeyer and Oekonomides (A., 1883, 201); the name isatinol should therefore be deleted from the literature and replaced by *iso*methylisatoid. Various formulæ for these substances are considered, but a definite conclusion does not yet seem possible.

[With MARIE MEYER.]—5-Chloroisatol, m. p. 188° (decomp.), is prepared by converting chloroisatin into the silver salt and treatment of the latter with benzoyl chloride in the presence of benzene; it does not react with phenylhydrazine or with methyl sulphate at 100°, is not basic, and is converted by hot alkali into chloroisatinic acid. 5-*Chloroisatin*-α(2)-*phenylhydrazone*, slender needles, m. p. 250° (decomp.), is prepared from phenylhydrazine and chloroisatin lactim ether, m. p. about 132°, after softening at 128° in alcoholic solution; the lactim ether yields chloromethylisatoid when subjected to illumination or heated with glacial acetic acid. 5-*Bromoisatol* is prepared in the same manner as the corresponding chloro-compound. The silver salt of 5-bromoisatin is primarily converted by methyl iodide in benzene solution at 100° into 5-bromoisatin lactim ether, which is subsequently partly transformed into 5-*bromo*-N-*methylisatin*, needles, m. p. 172—173° (more conveniently prepared by the action of alcoholic sodium methoxide on 5-bromoisatin), the conversion appearing to occur more readily than with the corresponding parent substances. 5-*Bromoisatin*-2-*phenylhydrazone* forms dark red, four-sided platelets, which decompose at 241—242°.

H. W.

Azopyrazolones and Allied Compounds. KENNETH HERBERT SAUNDERS (T., 1920, **117**, 1264—1272).

Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. III. Resolution of Phenylmethylethylazonium, Phenylbenzylpropylazonium, and Phenylbenzylallylazonium Iodides into Optically Active Components. BAWA KARTAR SINGH (T., 1920, **117**, 1202—1214).

Hydrazones and Azines. I. Coloured Ketazines. OTTO GERHARDT (*Monatsh.*, 1920, **41**, 199—214).—A number of ketazines have been prepared in the hope of tracing some connexion between colour and constitution in this class of substances. Even among the fluorenoneketazines, however, there seems to be no marked regularity; in spite of the presence of the chromophoric grouping, :C:N-, the close arrangement of the atoms in the molecule and the occurrence of crossed double bonds, the entrance of the auxochromic hydroxy-group in the meta-position causes only an unimportant deepening of the colour, but apparently no development of tinctorial power.

β-Hydrindoneketazine, pale pink needles, m. p. 194—195°, which undergo autoxidation on exposure to air, yielding dark red needles which could not be fully identified, is prepared by the action of hydrazine hydrate on an alcoholic solution of β-hydrindone. *2-Nitrofluorenonehydrazone* forms dark yellow, microscopic leaflets, m. p. 214°, and is oxidised by iodine in alcoholic solution to *2-nitrofluorenoneketazine*, brown, crystalline powder, m. p. 305—306°. *2-Aminofluorenonehydrazone*, orange-yellow, matted needles, m. p. 201—202°, is prepared from 2-aminofluorenone and hydrazine hydrate; it cannot be oxidised by iodine to the corresponding ketazine, nor can the latter be obtained from it by the action of a further molecule of the ketone. *2-Acetylaminofluorenone*, cinnabar-red crystals, m. p. 227—228°, is, however, readily convertible into *2-acetylaminofluorenonehydrazone*, lemon-yellow leaflets, m. p. 212—214°, which, when treated with iodine, gives *2-acetylaminofluorenoneketazine*, brown, crystalline powder, m. p. 303—306°; attempts to remove the acetyl groups from the latter were unsuccessful, since 2*N*-alcoholic potassium hydroxide solution was without action, whilst a saturated solution converted the substance into a viscous mass. *2-Dimethylaminofluorenone*, dark red, crystalline powder, m. p. 146—147°, is prepared in 40% yield by the action of methyl sulphate on the aminoketone at 170—180°, and is so extensively resinified by the action of hydrazine hydrate that the corresponding hydrazone could not be isolated. *2-Hydroxyfluorenonehydrazone*, chrome-yellow, matted needles, has m. p. 201—202°, whilst the corresponding *ketazine*, m. p. 301—303°, is a brown, crystalline powder. *Piperonaldazine*, m. p. 206—207°, crystallises in pale yellow leaflets. *Benzophenone-benzil-ketazine*, CPh_2:N·N:CPh·COPh, pale yellow crystals, m. p. 128—129°, is prepared from benzophenonehydrazone and benzil in the presence of a little alcohol at 150°, whilst *tetramethyldiaminobenzophenone-benzil-ketazine* forms orange-yellow leaflets, m. p. 173—174°.

H. W.

Ditertiary Hydrazines. XXII. Basic Tetra-arylhydrazines. HEINRICH WIELAND (*Ber.*, 1920, **53**, [*B*], 1313—1328. Compare A., 1915, i, 848, and previous abstracts).—The preparation of further substituted tetra-arylhydrazines has been attempted; the most noteworthy of the substances actually isolated is *pp'*-tetramethyldiaminodimethoxytetraphenylhydrazine,

$$(NMe_2{\cdot}C_6H_4)_2N{\cdot}N(C_6H_4{\cdot}OMe)_2,$$

in which the tendency towards dissociation is as marked as in the case of tetra-*p*-dimethylaminotetraphenylhydrazine.

[With J. SUREDA.]—pp'-*Diacetylaminotetraphenylhydrazine*, $NHAc{\cdot}C_6H_4{\cdot}NPh{\cdot}NPh{\cdot}C_6H_4{\cdot}NHAc$, colourless prisms, m. p. 124°, after slight decomposition from 100°, is obtained by the oxidation of *p*-acetylaminodiphenylamine by potassium permanganate in acetone solution; as is to be expected, the substance does not exhibit a strongly marked tendency towards dissociation, in which respect it resembles tetratolylhydrazine. Attempts to remove the acetyl groups without extensively decomposing the compound were unsuccessful.

[With E. SCHAMBERG.]—p-*Diethylaminodiphenylamine*, colourless leaflets, m. p. 88—89°, is obtained by the action of phenylhydrazine on *p*-nitrosodiethylaniline, and is converted by silver oxide in dry ethereal solution into *di*-p-*diethylaminotetraphenylhydrazine*, $NEt_2{\cdot}C_6H_4{\cdot}NPh{\cdot}NPh{\cdot}C_6H_4{\cdot}NEt_2$, m. p. 104° (darkening); in its tendency towards dissociation, the latter substance closely resembles tetra-anisylhydrazine. It is hydrolysed by water to diethylaminodiphenylamine, quinoneanil, and diethylamine. In benzene solution it readily unites with nitric oxide and triphenylmethyl to yield the *compounds*, $C_{16}H_{19}ON_3$, yellow needles, m. p. 78°, and $C_{35}H_{34}N_2$, coarse, colourless prisms, m. p. 163° (darkening), respectively.

[With FRL. E. HAAS.]—p'-*Dimethylamino*-p-*methoxydiphenylamine*, colourless leaflets, m. p. 78°, b. p. 200°/*ca.* 1 mm., is prepared by the action of *p*-iodoanisole, acetyldimethyl-*p*-phenylenediamine, potassium carbonate, copper bronze, and iodine in boiling nitrobenzene and subsequent hydrolysis of the primary product. When dissolved in a mixture of dry pyridine and ether and cooled in a freezing mixture of ice and salt, it is oxidised by silver oxide to pp'-*tetramethyldiaminodimethoxytetraphenylhydrazine*, quadratic prisms, m. p. 93°, after previous discoloration. Its solution in benzene readily absorbs nitric oxide with the formation of p'-*dimethylamino*-p-*methoxydiphenylnitrosoamine*, dark yellow leaflets, m. p. 95°.

[With E. SCHAMBERG.]—*Di*-pp'-*diethylaminodiphenylamine*, m. p. 56°, is prepared by reducing *p*-nitrosodiethylaniline with zinc dust, adding diethylaniline, oxidising with potassium dichromate, and reduction of the zinc double salt thus produced by hyposulphite. It differs from the corresponding tetramethyl base in that, as a consequence of extensive decomposition, it cannot be oxidised to the corresponding hydrazine; treatment with silver oxide in the presence of light petroleum transforms it into *diethylindophenol*, m. p. 106°.

Attempts to convert 2 : 4 : 6 : 2′ : 4′ : 6′-hexamethoxydiphenylamine into the corresponding hydrazine were unsuccessful. The substance is oxidised by silver oxide in acetone solution to *pentamethoxyquinoneanil*, $O:C_6H_2(OMe)_2:N\cdot C_6H_2(OMe)_3$, blackish-green, shining crystals, m. p. 202°, which is reduced by zinc dust and acetic acid to the corresponding leuco-*compound*, colourless needles, m. p. 156—157° (discoloration).

The oxidation of tetramethyldiaminodiphenylamine by an excess of silver oxide has been further studied, and the view taken previously that trimethylindamine [dimethylaminophenylmethylquinonedi-imide], $NMe:C_6H_4:N\cdot C_6H_4\cdot NMe_2$, is produced by the loss of hydrogen and methyl from the base is now abandoned, since it is found that the solution which has only been oxidised to the hydrazine stage contains only traces of the indamine. The latter owes its origin to the oxidation of the tetramethyldiaminodiphenyl nitrogen radicle,

$$NMe_2\cdot C_6H_4\cdot N\cdot C_6H_4\cdot NMe_2 \longrightarrow NMe_2\cdot C_6H_4\cdot N:C_6H_4:NMe + CH_3,$$

but the fate of the methyl radicle is not established. Isolation of trimethylindamine is most conveniently effected by treatment of the fully oxidised ethereal solution of tetramethyldiaminodiphenylamine with nitric oxide and separation of the *trimethylindaminedinitrosoamine*, yellowish-green crystals, m. p. 136° (decomp.) after softening at 130°. The latter is reduced by stannous chloride and concentrated hydrochloric acid to *trimethyldiaminodiphenylamine* colourless needles, m. p. 73°, which is oxidised by silver oxide in the presence of ether to *trimethylindamine*, m. p. 90°; nitric oxide and triphenylmethyl are readily added by the latter. H. W.

Ditertiary Hydrazines. XXIII. Mixed Aromatic Ditertiary Hydrazines. Tetrabenzylhydrazine. HEINRICH WIELAND and EDUARD SCHAMBERG (*Ber.*, 1920, **53**, [*B*], 1329—1335).—In continuation of previous work, the authors have now examined unsymmetrical diaryldialkylhydrazines, which, in regard to their tendency towards dissociation, are found to be even more stable than the corresponding symmetrical compounds. Attempts to prepare tetra-alkylhydrazines did not meet with success, but it has been found possible to isolate tetrabenzylhydrazine, which is found to possess extraordinary stability. It appears, therefore, that the instability of the N·N linkiug in hydrazines is conditioned by the immediate attachment of the nitrogen atoms to aryl groups, and that the phenomenon becomes more marked when positive groups are introduced into the nucleus.

as-*Diphenyldimethylhydrazine*, large, colourless prisms, m. p. 52°, is prepared by the action of methyl sulphate on *as*-diphenylhydrazine. It is more stable than the symmetrical isomeride, and remains unchanged when boiled for hours in xylene solution. It is more sensitive towards acids than is diphenylhydrazine, since it is converted by dilute aqueous hydrochloric acid into dimethylamine, diphenylamine, and a dye, which resembles emeraldine, and, as judged from its leuco-compound, $C_{26}H_{23}N_3$, m. p.

.75—176°, is composed of a molecule of diphenyldimethylhydrazine ınited with a molecule of diphenylamine.

Attempts to prepare tetramethylhydrazine are described, but he alkylation of hydrazomethane dihydrochloride by methyl-ılcoholic sodium hydroxide solution and methyl iodide only leads o the production of *N-methyl-N'-trimethylhydrazonium iodide*, $NHMe{\cdot}NMe_3I$, colourless prisms, m. p. 226·5°.

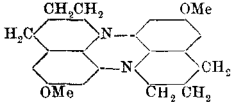
Tetrabenzylhydrazine, large, colourless prisms, m. p. 139·5°, is ırepared by the action of benzyl bromide on tribenzylhydrazine. t does not yield salts. It is unaffected by protracted treatment rith zinc dust and acetic acid, or by solution in concentrated ulphuric acid. When distilled under diminished pressure (260°/ 2 mm.), a portion passes over unchanged, whilst the remainder ı decomposed into dibenzylamine and benzylbenzylideneamine. t is smoothly converted by concentrated hydrochloric acid at 160° nto benzyl chloride and hydrazine.

[With FRL. E. HAAS.]—Attempts to convert di*cyclo*hexylamine ıto tetra*cyclo*hexylhydrazine were not successful, since a solu-on of the base in acetone was found to be fairly smoothly con-erted by permanganate into the cyclo*hexylamide* of adipic acid, $_6H_{11}{\cdot}NH{\cdot}CO{\cdot}[CH_2]_4{\cdot}CO_2H$, colourless needles, m. p. 138—139°, hich was identified by hydrolysis to adipic acid and *cyclo*hexyl-mine.

It is shown that two diphenylamino-radicles can be very firmly nited by the carbonyl group, since tetraphenylcarbamide remains nchanged when heated to 210°, and, in part, sublimes unaltered hen directly distilled. H. W.

Ditertiary Hydrazines. XXIV. Ditertiary Hydrazines f the Quinoline Series. HEINRICH WIELAND and EMMY HAAS Ber., 1920, **53**, [*B*], 1336—1343).—The similarity in properties etween tetrahydroquinoline and monoalkylated anilines has led ıe authors to attempt to obtain substances in which two quinolyl esidues are united by the nitrogen bond, and thus have a ɔrmal likeness to the ditertiary hydrazines. These substances re readily obtained by the direct oxidation of tetrahydroquinoline, .ethyltetrahydroquinoline, and *p*-methoxytetrahydroquinoline ith potassium permanganate; a similar compound could not, owever, be isolated in this manner from tetrahydro*iso*quinoline. he new "quinolinehydrazines" show little tendency towards dis-ociation, and give colourless solutions in boiling xylene; in solvents f higher boiling point, such as ethyl benzoate, the formation of ellow or brown solutions indicates the occurrence of dissociation, ut this only takes place under such conditions that the free ıdicles are extensively decomposed. They are not basic. They re more or less readily affected by acids. Thus, bistetrahydro-uinonyl is rapidly decomposed by ethereal or aqueous (25%) hydro-ıloric acid, with the formation of tetrahydroquinoline and esinification of the other half of the molecule. When an ethereal olution of the hydrazine is shaken with 2*N*-hydrochloric acid, a

benzidine transformation occurs smoothly, which must be regarded as an intramolecular change without previous dissociation. In those cases in which, for constitutive reasons, a benzidine transformation is impossible, total fission occurs; the latter type of change has been most closely studied with bis-1:2:3:4-tetrahydro-6-methoxyquinonyl, which is shown to yield 6-methoxy-1:2:3:4-tetrahydroquinoline (thallin) and thalloperazine (annexed formula).



The following compounds are described: *bis-1:2:3:4-tetrahydroquinolyl*, $C_9H_{10}\cdot N\cdot N\cdot C_9H_{10}$, large, yellow prisms, m. p. 141—142°; *tetrahydroquinobenzidine* [6:6′-*bis*-1:2:3:4-*tetrahydroquinolyl*], colourless needles, m. p. 128—129° [*dinitrosoamine*, golden rods, m. p. 196° (slight decomp.)]; N:N′-*bis*-1:2:3:4-*tetrahydro-6-methylquinolyl*, colourless needles, m. p. 107—108°; *thallinhydrazine*, m. p. 117—118° (slight decomp.); *thalloperazine*, yellow crystals, m. p. 160°, which when treated with ethereal hydrogen chloride, readily yields a meriquinonoid azonium *salt*. H. W.

Some Derivatives of 4-Nitro-*o*-toluidine. Alfred Godfrey Gordon Leonard and Agnes Browne (*Sci. Proc. Roy Dublin Soc.*, 1920, **16** [N.S.], 105—108).—When *p*-nitro-*o*-toluidine sulphate was diazotised in aqueous suspension and added to a cold alkaline solution of β-naphthol, 5-nitro-*o*-tolueneazo-β-naphthol, m. p. 204°, was obtained, which dyed cotton a deep orange colour. When the nitrotoluidine was diazotised and added to *o*-toluidine hydrochloride, *5-nitro-o-toluenediazoamino-o-toluene*, m. p. 133°, was obtained. *5-Nitro-o-toluenediazoamino-p-toluene*, m. p. 131° (decomp.), *5-nitro-o-toluenediazoaminobenzene-p-sulphonic acid*, m. p. 129° (decomp.); *5-nitro-o-toluenediazoamino-p-nitrobenzene*, m. p. 118° (decomp.) and *p-nitro-o-tolueneazoresorcinol*, m. p. 234°, were obtained in a similar manner. W. G.

O. Fischer's Bases from *p*-Nitrosoanilines and Arylhydrazines. Arylazohydroxyanilides [Aryldiazohydroxylaminobenzenes]. Eugen Bamberger (*Annalen*, 1920, **420**, 137—169).—O. Fischer and Hepp (A., 1888, 460) have described a peculiar class of substances obtained from *p*-nitrosoaniline, *p*-nitrosomonomethylaniline, and *p*-nitrosodimethylaniline on the one hand, and phenylhydrazine, α-methylphenylhydrazine, and diphenylhydrazine on the other, which they have termed diazobenzenenitrosoanilines (compare Fischer and Wacker, A., 1888, 1286; 1889, 702). Recently, Fischer and Johannes (A., 1915, i, 907) have pointed out that these compounds are simply the *p*-amino-substitution products of the diazoxyaminobenzenes obtained by Bamberger (A., 1918, i, 20; 1899, i, 589) by the con-

densation of diazonium salts with β-phenylhydroxylamine, and are best represented by one of the following formulæ:

$$NR_2\cdot C_6H_4\cdot NO\colon N\cdot NPhR'$$

or $NR_2\cdot C_6H_4\cdot N\overset{O}{\frown}N\cdot NPhR'$. The latter substances are obtained also from nitrosobenzenes and phenylhydrazines, and the formation of Fischer's bases is probably represented by the equations

$$2NH_2\cdot C_6H_4\cdot NO + 2H_2N\cdot NHPh = 2[H_2N\cdot C_6H_4\cdot N(OH)\cdot NH\cdot NHPh] = 2NH_2\cdot C_6H_4\cdot N(OH)\cdot N\colon NPh + 2H_2$$

and $H_2N\cdot C_6H_4\cdot NO + 2H_2 = C_6H_4(NH_2)_2 + H_2O$. Substituted and unsubstituted nitrosoaryls yield arylazohydroxyanilides [diazohydroxylaminobenzenes] with primary arylhydrazines and arylazoanilide oxides with secondary hydrazines.

[With Alexander Landau, K. Blaskopf, E. Hindermann, and H. Büsdorf.]—Benzenediazohydroxylamino-*p*-dimethylaminobenzene, $NMe_2\cdot C_6H_4\cdot N(OH)\cdot N\colon NPh$ (Fischer and Wacker, *loc. cit.*), decomposes at different temperatures, 113° or 119°, according to the rate of heating (the *copper* salt is described); attempts to methylate it with methyl sulphate and potassium hydroxide led to the formation of tetramethyldiaminoazobenzene, and, possibly, a small amount of the desired ether, m. p. 135—142° (decomp.). Benzenediazohydroxylamino-*p*-aminobenzene yields a bluish-green *copper* salt, *decomposing with explosion at 186—187°*, and, when pure, yields colourless salts with acids; with potassium ethoxide solution, a yellow *potassium* salt is produced, which is hydrolysed by water.

Diazohydroxylaminobenzene is rapidly decomposed by boiling concentrated hydrochloric acid into nitrogen, phenol, and *p*-chloroaniline. When treated with potassium ethoxide and methyl sulphate, it yields acetaldehyde, benzene, and azobenzene, whilst the latter is also obtained when methyl iodide is used; it is unaffected by diazomethane. Zinc dust and acetic acid reduce it to aniline and phenylhydrazine. The presence of the hydroxyl group cannot be established by means of sulphur dioxide (as in the case of phenylhydroxylamine), since aniline and benzenediazonium sulphate are formed. *p*-Toluenediazohydroxylaminobenzene is similarly reduced to aniline and *p*-toluenediazonium sulphate.

p-*Nitrobenzenediazohydroxylaminobenzene*, from diazotised *p*-nitroaniline and phenylhydroxylamine, forms slender, pale yellow needles, which *decompose at 175°, or at 185°* when placed in a bath pre-heated to 174°; the *potassium* and *sodium* salts are described. Attempts to prepare the methyl ether were not successful, the sole product isolated being *p*-iodonitrobenzene.

The decomposition of isomeric aryldiazohydroxylaminobenzenes, $R\cdot N_2\cdot N(OH)R'$ and $R'\cdot N_2\cdot N(OH)R$, by mineral acids has been investigated in a number of cases. p-*Tolueneazohydroxylaminobenzene*, sulphur-yellow needles, which rapidly become brown on

exposure to sunlight, m. p. 130—131° (decomp.), is converted b sulphuric acid into nitrogen, *p*-cresol, and phenylhydroxylamin (or *p*-aminophenol), whilst benzenediazohydroxylamino-*p*-toluen m. p. 123·5—124°, yields nitrogen, phenol, and *p*-tolylhydroxy amine (or toluquinol). Similarly, *benzenediazohydroxylamino-*p *bromobenzene*, golden needles, grouped in clusters, m. p. 128·5° gives nitrogen, phenol, *p*-dibromoazoxybenzene, and *p*-bromoanilin (the latter two being derived from *p*-bromophenylhydroxylamine) whilst *p*-bromobenzenediazohydroxylaminobenzene, straw-yello needles, m. p. 154·5°, is decomposed into nitrogen, *p*-bromophenol and phenylhydroxylamine. p-*Toluenediazohydroxylamino*-p-*bromo benzene*, greenish-yellow, matted needles, decomposing at 122—123° when slowly heated, but at 134° when placed in a bath pre-heate to 100°, is transformed by dilute hydrochloric acid into *p*-cresol *pp'*-dibromoazoxybenzene, *o*-chloro-*p*-bromoaniline, and *p*-bromo aniline (the three substances last named being derived fron *p*-bromophenylhydroxylamine), whereas p-*bromobenzenediazohydr oxylamino*-p-*toluene*, greenish-yellow needles, which decompose a 151°, is decomposed by boiling dilute sulphuric acid into nitrogen toluquinol, and *p*-toluidine.

Fuller details are given with regard to the action of phenylhydrazine on nitrosoaryls. In general, the substances are mixed in alcoholic solution at 0°, when action occurs with greater or less rapidity, accompanied by slight, but persistent, evolution of gas In this manner, nitrosobenzene and phenylhydrazine yield diazohydroxylaminobenzene, phenylhydroxylamine, and, probably, azobenzene. *p*-Tolylhydrazine gives *p*-toluenediazohydroxylaminobenzene and phenylhydroxylamine, whilst the isomeric anilide and *p*-tolylhydroxylamine are obtained from *p*-nitrosotoluene and phenylhydrazine. *p*-Bromonitrosobenzene and phenylhydrazine yield benzenediazohydroxylamino-*p*-bromobenzene and *p*-bromophenylhydroxylamine (or *pp'*-dibromoazoxybenzene and *p*-bromoaniline). H. W.

Does Gliadin contain Amide Nitrogen? THOMAS B. OSBORNE and OWEN L. NOLAN (*J. Biol. Chem.*, 1920, **43**, 311—316).—Boiling gliadin with 1% hydrochloric acid for two hours yields almost as much ammonia as boiling for twenty-four hours with 20% acid. The slight increase in free amino-nitrogen after boiling with the dilute acid shows that a very slight hydrolysis of peptide linkings occurs. Since upwards of 90% of the ammonia is yielded at a rate strictly proportional to the time of boiling, as well as the concentration of the acid, it seems fair to assume that nearly all the ammonia originates from a common group, which, like $R-CO\cdot NH_2$, is very readily hydrolysed.

There is also an increase in acidity during the mild hydrolysis which corresponds with carboxyl groups nearly, if not quite, equivalent to the ammonia produced.

The uramino-group would appear to be present in extremely small amounts, if at all, in gliadin. J. C. D.

Oxygen-capacity of Hæmoglobin. R. Wertheimer (*Biochem. Zeitsch.*, 1920, **106**, 12—22).—Measurements made by means of a Barcroft's differential apparatus show that, in a solution rendered alkaline by addition of sodium carbonate, 1 gram of hæmoglobin fixes at the ordinary temperature and under medium atmospheric pressure 1·33 c.c. of oxygen, which is almost the exact quantity required by Hüfner's assumption that the hæmoglobin and oxygen combine in molecular proportions (A., 1893, i, 616). With a pure, aqueous solution of hæmoglobin, the proportion of oxygen combined is about 7% less than that given above.

T. H. P.

A New Hæmatin-like Crystalline Substance. S. Partos (*Biochem. Zeitsch.*, 1920, **105**, 49—59).—By heating defibrinated blood containing 1% of sodium sulphate, pressing the coagulum, washing it with hot water, again pressing it, and extracting with 92% methyl alcohol containing 5% of formic acid, the author has obtained a substance crystallising mostly in short needles. In some of its characters, this substance agrees with hæmatin, but it contains only 7·41—8·00% of iron, whereas hæmatin contains 8·9%; furthermore, the maxima of light-absorption in the two cases do not correspond. T. H. P.

Calorimetric Investigations on Melanins. II. Franz von Hoefft (*Biochem. Zeitsch.*, 1920, **106**, 207—211).—Further observations are described supplementing those previously made (this vol., i, 686). T. H. P.

Hydrolysis of Nucleotides. M. Yamagawa (*J. Biol. Chem.*, 1920, **43**, 339—353).—Early in the work on nucleotides, it was observed that these compounds differed from one another in their resistance to hydrolysis.

Since it is possible that the nucleotides differ in the position at which the phosphoric acid radicle is attached to the carbohydrate group, it was decided to compare the rates of hydrolysis of a number of these compounds (compare this vol., i, 712). In only one compound of this type, inosic acid, is the position of the phosphoric acid known, namely, linked to the fifth carbon atom. The rates of hydrolysis by $0\cdot1N$-sulphuric acid at 100° in a sealed tube were studied. The unimolecular law was followed, and the following constants, K, were obtained:

	K.
Nucleic acid	130 (10^{-2})
Guanosinephosphoric acid	177 (10^{-2})
Adenosinephosphoric acid	166 (10^{-2})
Uridinephosphoric acid	480 (10^{-2})
Inosic acid	470 (10^{-2})
Hexathymidinediphosphoric acid	726 (10^{-2})

Thus the velocity-constants of the guanosinephosphoric and the adenosinephosphoric acids are identical. On the other hand, the constants of inosic and uridinephosphoric acids are also identical,

in spite of the fact that their basic component is of a differe nature. J. C. D.

Structure of Yeast-nucleic Acid. Ammonia Hydrolysis the so-called Trinucleotide of Thannhauser an Dorfmüller. P. A. Levene (*J. Biol Chem.*, 1920, **43**, 379—382).—A previous communication (this vol., i, 193) has dealt with th theoretical arguments against the conception of the structure yeast-nucleic acid suggested by Thannhauser and Dorfmüller (A 1918, i, 47). In order to support these criticisms with eviden obtained from actual experiment, the author has shown that th conditions of hydrolysis employed by Thannhauser and Dorfmüll are such as to produce a mixture of mononucleotides, and not trinucleotide. J. C. D.

The Occurrence of Optical Antipodes in Nature. Ha Pringsheim (*Ber.*, 1920, **53**, [*B*], 1372—1374).—In a recent co munication, Hess and Weltzien (this vol., i, 328) have adduce arguments which lead them to the conclusion that a fundament difference exists between chemical processes in the vegetable an animal kingdoms, and that whereas the animal organism on builds and degrades asymmetrically, and hence involves enzym of asymmetric structure, the vegetable organism can also bui symmetrically, and hence involve symmetrical enzymes. Th author considers this statement to be too general, and points ou that racemic substances are also formed, if exceptionally, in th animal organism, and cites, as example, the occurrence *dl*-arabinose in certain urines. On broader grounds, he conside that the specific action of an enzyme is only conditional, and th whilst a ferment preferentially attacks one modification of a give compound, it can, in case of necessity, also attack the antipod So rigid a classification of symmetrical and asymmetrical fermen does not appear to have been attempted previously, and unt more is known of the chemical structure of ferments, it appea too early to assume that steric arrangements must of necessity b present in them as in the substrates. H. W.

The Ability of Plants to Form Optical Antipodes. Kur Hess (*Ber.*, 1920, **53**, [*B*], 1375—1378. Compare Hess an Weltzien, this vol., i, 328).—A reply to Pringsheim (precedin abstract). Although noting that exceptions to Fischer's rule a much more common among plants and the lower organisms tha among animals, the author admits that his suggestion of "fundamental difference between the vegetable and the anim organism" is possibly too general. He considers, however, th there is abundant evidence of the asymmetric molecular structu of enzymes, and supports his contention by arguments based on th work of van't Hoff, E. Fischer, Bredig, Rosenthaler, an Bourquelot and Bridel. H. W.

The Chemical Nature of Enzymes. Th. Bokorny (*Biochem*

estimated in a number of well-known enzymes by means of nitrous acid. The amino-nitrogen was found to vary from 3·05% in rennet to 7·66% in papayotin. The author considers that the results obtained are in favour of the theory of the protein nature of enzymes. S. S. Z.

Destruction of Rennet and Pepsin by Alkali. L. MICHAELIS and M. ROTHSTEIN (*Biochem. Zeitsch.*, 1920, **105**, 60—87).—The method used to arrive at a quantitative measure of these two enzymes consists in determining by trial that dilution of the enzyme solution which corresponds in its activity with a control solution prepared so as to be readily reproducible. The action was measured by means of the coagulation of milk containing calcium chloride in the case of rennet, and by the gradual clearing of an albumin solution rendered turbid by addition of sulphosalicylic acid in the case of pepsin.

If the hydrogen-ion concentration of a rennet solution is adjusted by means of a mixture of phosphates, the enzyme remains practically unrestricted with an acid reaction down to $p_H=6$. As neutrality is approached, a rapid destruction of the enzyme suddenly begins, the velocity of the destruction quickly becoming immeasurably great as the value of p_H diminishes further. For a given value of p_H, the destruction of rennet is not a unimolecular reaction, the velocity of the destruction at any moment being proportional to the 1·5th power of the amount of enzyme still present; the course of the destruction is not influenced by the enzyme already destroyed. For a given quantity of enzyme, the velocity of the destruction is proportional inversely to the fourth power of the $H^{\cdot}$-concentration, or directly to the fourth power of the OH'-concentration.

As regards the velocities of destruction at different temperatures (25·5° and 36·8°), these are identical if the solutions compared are of equal concentrations of hydroxyl ions, that is, the "physical" temperature-coefficient of the velocity is practically zero. When, however, the concentration of the hydrogen ions is the same in the two solutions, the velocity of destruction at 36·8° is thirty-one times that at 25·5°, so that the "physiological" temperature-coefficient is of considerable magnitude. From the purely physical point of view, the former method of formulation is the more correct, since the hydroxyl ions represent the destroying agency; the other method is, however, of the greater physiological importance, because in the fluids of the body the concentration of the hydrogen ions, but not that of the hydroxyl ions, is almost independent of the temperature.

Destruction of pepsin by hydroxyl ions always proceeds proportionally to that of rennet, no disproportionality being observable, even after partial adsorption of the enzyme solution by kaolin. The kinetics of the reaction is expressed empirically by the equation $-dx/dt=k\,.\,x^{\frac{3}{2}}\,.\,[OH']^4$, where x represents the quantity of enzyme present at time t. T. H. P.

The Influence of Neutral Alkali Salts on Diastati Enzymes. I. AMANDUS HAHN and KARL HARPUDER (*Zeitsch Biol.*, 1920, **71**, 287—301).—The optimum H-ion concentration fo the activity of ptyalin is $p_H = 6 \cdot 4$—$6 \cdot 5$, and for that of malt diastas $p_H = 4 \cdot 7$. The enzymic activity is not only influenced by th H-ion concentration of the buffers, but by the concentration of th other ions contained in them. The combination of neutral alka salts with the buffers produces either an accelerating or inhibitin influence, according to the reaction and concentration of the salt and buffers, on the activity of the enzymes. The optimum H-io concentration is also changed by the combined influence of th neutral salts and the buffers. S. S. Z.

The Influence of Neutral Alkali Salts on Diastati Enzymes. II. AMANDUS HAHN and KARL HARPUDER (*Zeitsc Biol.*, 1920, **71**, 302—310).—Neutral alkali salts move the isoelectri point of ptyalin and malt diastase in the acid direction. Th influence of sodium salts in this respect is more marked than tha of potassium salts. The mode of action of the above enzymes i independent of their electrical nature. S. S. Z.

The Process of Purifying Pancreatic Amylase H. C. SHERMAN, I. D. GARARD, and V. K. LAMER (*J. Amer Chem. Soc.*, 1920, **42**, 1900—1907).—A further study of th process of purification of pancreatic amylase previously describe (compare A., 1911, i, 827), a determination of the total solids an enzyme activity being made at each stage. It was found tha alcohol up to 5%, or an alcohol-ether mixture up to 8%, of th volume of the substrate did not materially affect the activity c the pancreatic amylase. When extracts of pancreatin in 50% alcohol were precipitated by an alcohol-ether mixture, the residua solution contained about 1% of the active amylase and 2·5% of th solids of the original pancreatin, or about 5% of the solids origin ally extracted. When this precipitate was dispersed in water an mixed with alcohol, the filtrate showed no amylolytic activity although it contained 25% of the solids originally extracted. I the process of purification used, about 50% of the amylolytic activit was lost by the end of the dialysis, but by using liquid-air cooling it was possible in other experiments considerably to increase th proportion of active amylase recovered in the final product. Th precipitate ("sac precipitate") which formed in the inner solutio during dialysis showed very high proteolytic and little or n amylolytic activity. W. G.

Influence of Neutral Salts on Ferment Action S. M. NEUSCHLOSZ (*Pflüger's Archiv*, 1920, **181**, 45—64; from *Chem. Zentr.*, 1920, iii, 355. Compare this vol., i, 698).—Investi gation of the influence of neutral salts, singly and in conjunction on the fission of sucrose by invertase on the one hand and on th surface tension of invertase solutions on the other, leads to th conclusion that the restrictive action of neutral salts on ferment ative activity depends on a diminution of the dispersivity and c

he active surface of the ferment. The antagonism of ionic actions owards fermentation is shown in the diminution of the coefficient, K, of the adsorption isotherm for the action of cations in mixtures of salts; when the antagonism is maximal, this has its minimal value. H. W.

Decomposition of Tyrosinase into Components. Hugo Haehn (*Biochem. Zeitsch.*, 1920, **105**, 169—192).—Further experiments have been made in order to ascertain to what salts the activating effect of the ash of the ultra-filtrate on α-tyrosinase is due (compare this vol., i, 102).

The action of tyrosinase proceeds best when the reaction of the solution is approximately neutral, hydroxyl ions and the hydrogen ions of acetic, lactic, and hydrochloric acids exerting a retarding influence. Salts of a number of metals have been investigated, and it is found that zinc, cadmium, and calcium ions cause the most marked activation of α-tyrosinase, and surpass in their action the ash of the ultra-filtrate itself. The phosphoric anion also strongly activates α-tyrosinase. The latter is an organic substance which undergoes decomposition only at 80°, and is not decomposed by proteolytic enzymes.

Tyrosinase must be regarded as a mixture of enzymes. According to various investigators, the tyrosine is first decomposed by means of the aminoacidase in the sense of Strecker's equation, the phenolase then introducing a hydroxyl into the benzene nucleus. Subsequently, the melanin molecule is developed by the action of condensing enzymes, these being activated by metallic salts. It is *to such salts that melanin owes its characteristic coloration.* T. H. P.

Organic Compounds of Arsenic. I. Reaction between the Grignard Reagent and Arsenious Chloride. Kaoru Matsumiya (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 217—223).—When arsenious chloride acts on magnesium phenyl bromide in ethereal solution in equimolecular proportions, the product is triphenylarsine if the former is added gradually to the latter. If, however, magnesium phenyl bromide is added to arsenious chloride, the product is diphenylchloroarsine. Under similar conditions, magnesium α-naphthyl bromide gives *tri-α-naphthylarsine*, m. p. 248°, and *di-α-naphthylchloroarsine*, m. p. 116—117°, respectively. W. G.

The Theory of Electrolytic Ions. XVII. The Conductivity of the Sodium Arsinates. Richard Lorenz and Erika Schmidt (*Zeitsch. anorg. Chem.*, 1920, **112**, 209—220).—The conductivities of the sodium salts of a number of substituted phenylarsinic acids have been measured at *dilutions from 23 to* 1024, and the limiting conductivities at infinite dilution have been calculated *from* the two Kohlrausch extrapolation formulæ, $\mu_\infty - \mu = a[S_0]^{\frac{1}{2}}$ and $\mu_\infty - \mu = b[S_0]^{\frac{1}{3}}$ (compare this vol., ii, 6). The smallest conductivities were shown by the neutral monosodium salts of amino-substituted acids, for example, sodium arsanilate,

o-aminotolylarsinate, *oo'*-diaminodiphenylarsinate, and dimethylaminophenylarsinate, the mono-acid salts of bivalent acids, such as dichloro- and dibromo-hydroxyphenylarsinic, *m*-dihydroxyphenylarsinic, and the di-acid salt of 3-nitro-4-hydroxyphenylarsinic acid (μ_{∞} = 75—100). A second group, μ_{∞} = 100—200, comprised the neutral salts of bivalent acids, such as those mentioned above and the mono-acid salts of tribasic acids. Higher conductivities were shown by the neutral salts of the tribasic acids, 3-nitro-4-hydroxyphenylarsinic acid (329) and dinitrohydroxyphenylarsinic acid (330), by the mono-acid salt of phenylene-1:4-diarsinic acid (287), and the neutral salt of the same acid (392). The aminophenylarsinic acids are probably monobasic through internal ring formation between the amino-group and the arsinic acid residue.

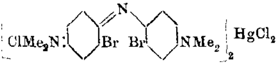
E. H. R.

Compounds of Arsenic Acid and Catechol. II. R. F. WEINLAND and J. HEINZLER (*Ber.*, 1920, **53**, [*B*], 1358—1368).—The authors have described previously the preparation of catechol semiarsenate, $AsO(O\cdot C_6H_4\cdot OH)_3,4H_2O$, and certain of its salts (A., 1919, i, 442); additional compounds of the acid are now discussed.

Catechol semiarsenate forms rhombic bipyramidal crystals, $a:b:c = 0.958:1:0.988$ (the *dihydrate*, dimethyl alcoholate, colourless rods, and diethyl alcoholate, long, colourless, flat prisms, are described); the free acid is hydrolysed by water, about 36% of the substance being present unchanged in 5% aqueous solution. The following salts are described, in which (as in the previous examples) the acid is monobasic unless the contrary is specifically stated: *lithium* salt ($+4H_2O$), shining, stout, four-sided plates; *mercurous* salt, $\left[AsO(O\cdot C_6H_4\cdot O)_3\right]^{Hg_2}_{H}$, dark brown, crystalline powder, which becomes yellowish-brown on exposure to air, owing to the absorption of about 1% of water; *thallium* salt, ice-like crystals; *chromium* salt ($+12H_2O$), greenish-black cubes; *aluminium* salt ($+12H_2O$), cubes; *cerium* salt ($+15H_2O$), colourless needles; *lanthanum* salt ($+15H_2O$), colourless needles; *yttrium* salt ($+15H_2O$), colourless needles; *hexamminecobalti*-salt, $\left[AsO(O\cdot C_6H_4\cdot O)_3\right]^{Co(NH_3)_6}_{3H_6}$, four-sided, yellowish-brown leaflets; *aquopentamminecobalti*-salt, acute, four-sided, brownish-red leaflets; *chloropentamminecobalti*-salt, short, copper-red rodlets; *aquopentamminenickeli*-salt, rhombic, lilac platelets; *monopyridine* salt, colourless, crystalline powder; *dipyridine* salt, stout, well-formed prisms, which continuously evolve pyridine; *monoquinoline* salt, yellowish-white powder (the salt is so sparingly soluble that, under definite conditions, it can be utilised in the gravimetric estimation of quinoline); *salt* with 1·5 molecules of quinoline, yellow, pointed rods; *monoaniline* salt, rods or pyramids; *dianiline* salt, stout, rectangular plates or rods; *guanidine* salt, colourless crystals resembling magnesium ammonium phosphate.

As is to be expected from its behaviour with pyridine and quinoline, catechol semiarsenate yields sparingly soluble salts with the alkaloids; this has been demonstrated in the cases of morphine, *quinine*, strychnine, colchicine, hydrastinine, veratrine, coniine, and *apo*morphine. H. W.

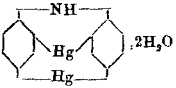
Aromatic Mercuri-organic Derivatives. MORRIS S. KHARASCH and JEAN F. PICCARD (*J. Amer. Chem. Soc.*, 1920, **42**, 1855—1864).—Methods are outlined for the preparation of a six-atom heterocyclic ring containing mercury in place of a non-metal. By the action of methyl sulphate on *m*-bromoaniline in the presence of sodium carbonate, a mixture of *m*-bromomethylaniline and *m*-bromodimethylaniline was obtained, from which, by treatment with sodium nitrite and hydrochloric acid, *m*-bromo-*p*-nitrosodimethylaniline and m-*bromophenylmethylnitrosoamine*, m. p. 49°, were obtained. By reduction with stannous chloride and hydrochloric acid, *m*-bromo-*p*-nitrosodimethylaniline yielded m-*bromodimethyl*-p-*phenylenediamine dihydrochloride*, giving the free *base*, m. p. 47·5°. The free base, when mixed with *m*-bromodimethylaniline and the mixture oxidised with potassium dichromate in hydrochloric acid solution, gave, on the addition of zinc chloride, *oo'-dibromo-Bindschedler's green*, $C_{32}H_{36}N_6Br_4Cl_2,ZnCl_2$, from which, by addition of mercuric chloride, the double *mercuric chloride* salt (annexed formula) was obtained.



m - Bromophenylmethylnitrosoamine, when dissolved in a mixture of ether and alcohol and the solution saturated with hydrogen chloride, underwent molecular rearrangement, giving m-*bromo*-p-*nitrosomethylaniline hydrochloride*, m. p. 168°, from which the free *base* was obtained.

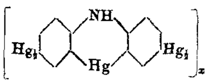
o-Chloromercuriphenol, when treated with nitrous acid, yielded p-*nitroso*-o-*chloromercuriphenol*, $OH\cdot C_6H_3(NO)\cdot HgCl$, which, when warmed with ammonium chloride, ammonium acetate, and ammonium carbonate, gave p-*nitroso*-o-*chloromercurianiline*.

When heated with mercuric chloride, diphenylamine yielded *tetrachloromercuridiphenylamine*, $NH[C_6H_3(HgCl)_2]_2$, from which, by the action of sodium thiosulphate, 3:3'-*mercurimercazine* (formula I or II) was obtained.



(I.)

or



(II.)

When tetrachloromercuridiphenylamine was warmed with a mixture of sulphuric and nitric acids, *dinitro*-2:2':3-*trichloromercuridiphenylamine* was obtained, which, by the action of sodium thiosulphate, yielded *mercury-bis-3-dinitro(?)-mercazine*. W. G.

g g**

Mercuration. V. Mercuration of Phenol Ethers. W. MANCHOT and F. BÖSSENECKER (*Annalen*, 1920, **421**, 331—345).—Volhard and Dimroth have shown that the mercuration of derivatives of benzene occurs in such a manner that a hydrogen atom attached to the ring is replaced by the group HgX. The authors' work on the mercuration of ethylene and its derivatives has, however, rendered it not improbable that the primary products are additive compounds. Experiments with various phenol ethers tend to show that such is actually the case. The products obtained with mercuric acetate vary with the particular ether used, but may be classified as more or less completely hydrolysed additive compounds. They are readily decomposed by treatment with warm dilute hydrochloric acid, and are immediately converted by alkali haloids into products which are mercurated in the nucleus.

p-Tolyl methyl ether slowly reacts with aqueous mercuric acetate solution at 50°, giving the *substance*,

$$3C_6H_4Me\cdot OMe\cdot Hg(C_2H_3O_2)_2,2HgO,$$

thin, colourless needles, m. p. 132—133°, immediately transformed by sodium chloride solution into the *product*, $C_6H_3Me\cdot OMe\cdot HgCl$, colourless needles, m. p. 162°. Similarly, anisole yields the *compound*, $C_7H_8O,Hg(OH)_2$, slender needles, m. p. 173°, which forms anisole when treated with dilute hydrochloric acid, and *p*-anisylmercuri-chloride, m. p. 236—237°, under the action of sodium chloride. In like manner, phenetole gives the *substance*,

$$OEt\cdot C_6H_5,Hg(OH)_2,$$

small, matted needles, m. p. 135·5°, which is converted by potassium bromide into *p*-phenetylmercuri-bromide, needles, m. p. 238°. H. W.

Physiological Chemistry.

Hydrogen-ion Measurements on Blood in the Neighbourhood of the Isoelectric Point of Hæmoglobin. T. R. PARSONS and WINIFRED PARSONS (*Proc. Physiol. Soc., J. Physiol.*, 1920, **53**, c—cii).—The view having been elaborated that, under physiological conditions, hæmoglobin is an acid of sufficient strength to expel carbon dioxide from sodium hydrogen carbonate at low tensions of the gas, it became of interest to observe the changes in its acid properties as the reaction of the medium in which it occurs approaches the isoelectric point. There is a sudden increase in carbon dioxide combining power in completely reduced hæmolysed blood, similar to that noted by Straub and Meier (A., 1918, ii, 467; 1919, i, 53) in acidified oxygenated whole and hæmolysed blood at a certain hydrogen-ion concentration not far removed from neutral point.

Hydrogen-ion measurements were made at various tensions of carbon dioxide, and these results show that over a certain range, depending on the exact amount of lactic acid present, the hydrogen

ion of the hæmolysed blood remains constant. It therefore appears that during this sudden increase of carbon dioxide combining power near the neutral point, the extra carbon dioxide is taken up in the form of sodium carbonate, and does not combine directly with hæmoglobin.

The reason why one molecule of extra carbon dioxide corresponds with each molecule of hæmoglobin seems to be that each hæmoglobin molecule is parting with one atom of available sodium for the formation of bicarbonate. It should be noted that this region of constant hydrogen-ion concentration is still on the alkaline side of the isoelectric point of hæmoglobin. J. C. D.

Occurrence of Creatinine and Creatine in the Blood in Healthy and Pathological Cases. IV. Revision of Previous Methods and Results. JOH. FEIGL (*Biochem. Zeitsch.*, 1920, **105**, 255—281. Compare A., 1918, i, 202, 357).—The considerations here presented show that the numbers obtained by Folin's older method for the proportion of pre-formed creatinine in the blood are to be regarded as trustworthy, but that the results obtained by American and German investigators for creatine are valueless. Revised procedure is described, and new results given for blood of healthy and diseased subjects. T. H. P.

The Appearance of Aldehyde-like Substances in the Blood of Six Persons (Diabetes Mellitus, Diseases of the Kidneys). WILHELM STEPP (*Biochem. Zeitsch.*, 1920, **107**, 60—80).—The presence of substances possessing the properties of aldehydes was established in the blood of some diabetic, nephritic, and other patients. These substances form iodoform with iodine in alkaline solution, and reduce Fehling's solution as well as ammoniacal silver, and give a red coloration with magenta-sulphurous acid. They are destroyed on being heated with silver oxide. In certain cases, the Rimini reaction was also obtained. The above reactions were also obtained from distillates in alkaline solution. S. S. Z.

Physiology of Blood Sugar. III. The Residual Reduction of Blood. RICH. EGE (*Biochem. Zeitsch.*, 1920, **107**, 229—245. Compare A., 1918, i, 356; ii, 278).—The residual reducing capacity of blood can be estimated by fermenting the reducing sugars with yeast. The reducing capacity of the yeast, as well as its activity, must be taken into consideration. The residual reduction of blood as estimated by Bang's micro-method is extremely small, and is of the same order in the plasma as in the corpuscles. Arterial and venous blood also show the same residual reduction. S. S. Z.

The Chemistry of the Blood-colouring Substances. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1919, **100**, 64—80).—According to the authors, there is only one substance, *haemochrome*, which is responsible for the colour of blood. It is an amorphous powder, which exists in colloidal solution in water. In alcohol and bicarbonate, on the other hand, it exists in real

solution. The spectroscopic behaviour of hæmochrome is influenced by the solvent in which it is dissolved. Hæmoglobin is hæmochrome adsorbed by globin. S. S. Z.

The Biochemistry of Phosphatides and Sterols. I R. Brinkman and (Frl.) E. van Dam (*Biochem. Zeitsch.*, 1920, **108**, 35—51).—The osmotic resistance of blood corpuscles raised by washing them with a physiological salt solution (0·85% NaCl) is due to the removal of the adhering lecithin, which is adsorbed by them from the plasma, and which is responsible for lowering their osmotic resistance. Cholesterol has the opposite effect. An isotonic sucrose solution does not remove the adhering lecithin. The analogy between the properties of the plasma lecithin and the serum complement, as well as its relation to the middle piece of the complement, is discussed. A method for the estimation of the osmotic resistance of the corpuscles under various conditions is described. S. S. Z.

The Biochemistry of Phosphatides and Sterols. II. The Importance of Cholesterol for the Physico-chemical Properties of Cell Surface. R. Brinkman and (Frl.) E. van Dam (*Biochem. Zeitsch.*, 1920, **108**, 52—60).—It has been pointed out by Hamburger (*Pflüger's Archiv*, 1895, **141**, 230) and others that erythrocytes in salt solutions become spherical. The authors show that the slightly negative charge of the corpuscle is augmented by being in contact with the charged slide, and this increase in the charge is responsible for the change in form of the erythrocyte. In the plasma the corpuscles are surrounded by a layer of lecithin containing cholesterol in colloidal solution, which prevents the cell from being acted on by an electric charge, and therefore their shape is not altered. S. S. Z.

The Biochemistry of Phosphatides and Sterols. III. The Significance of the Functional Antagonism between Phosphatides and Cholesterol. R. Brinkman and (Frl.) E. van Dam (*Biochem. Zeitsch.*, 1920, **108**, 61—73).—Phosphatides and sterols are always present in the animal organism in definite proportions, because they function antagonistically to each other. The relative amounts of cholesterol and lecithin influence the resistance of the corpuscles, the electrical isolation of the cells, the permeability to ions of the cell surface, and the water content of the tissues. The change in quotient of these two constituents, especially through the agency of nutrition, is of importance. A one-sided administration of lecithin to a rabbit has produced intensive hæmolysis in vivo, as well as regeneration of the blood corpuscles. S. S. Z.

Action of Electrolytes on Ricin-Hæmagglutination. Peter Rona and Paul György (*Biochem. Zeitsch.*, 1920, **105**, 120—132).—The results of the authors' experiments show that the agglutination of blood corpuscles by ricin takes place solely in presence of electrolytes. The cations may be arranged in the

'ollowing series, the first having the least and the last the greatest effect on the agglutination: K, Na, Ba, also Mg, Ca. Contrary to the statements of various authors, the agglutination is influenced differently by different anions; in the series Cl, SO_4, NO_3, phosphate anion, $FeCy_6$, SCN, I, the first aids agglutination the most and the last the least. The results obtained are in agreement with Freundlich and Rona's theory, according to which the sensitisation of blood corpuscles depends on diminution of their electric charge. Roughly quantitative investigation of the cataphoretic velocities of blood corpuscles charged with ricin, and others uncharged, appeared to indicate no certain difference between these velocities.

T. H. P.

Preparation and Investigation of Thrombin. MAX BLEIBTREU and EDGAR ATZLER (*Pflüger's Archiv*, 1920, **181**, 130—140; from *Chem. Zentr.*, 1920, iii, 420).—Acetic acid is added to the serum (100 c.c.), which has been agitated with casein (1 gram), whereby the latter is precipitated, together with the adsorption compounds which it forms, with thrombin and metathrombin. The preparation is stable when dried and powdered, and does not lose its activity when preserved during a year. Active and stable thrombin solutions can be prepared from it by treatment with water and *N*-sodium hydroxide solution, neutralisation with *N*-hydrochloric acid, and purification by precipitation with colloidal ferric hydroxide, saturated magnesium sulphate solution, and alcohol (one-third to one-half volume), and these solutions have been found useful in treating hæmorrhage in animals. In an electric field, thrombin and metathrombin migrate to the anode.

H. W.

Mechanism of Pepsin Action. A. GYEMANT (*Biochem. Zeitsch.*, 1920, **105**, 155—168).—The author discusses the two principal theories of the action of pepsin, especially that according to which the function of the acid is to cause the protein to swell, and so become accessible to the enzyme. When hydrochloric acid is used, the "protein chloride" is usually a strongly dissociated electrolyte, so that, as the acidity increases to a moderately high value, the number of protein ions and the swelling must increase. This is, however, not always the case, since with serum albumin + sulphosalicylic acid, and with ricin globulin + sulphosalicylic acid, the acid causes, not swelling, but precipitation, of the protein. Digestion experiments with the heterogeneous systems thus obtained show that the optimal acidity is $p_H = 1 \cdot 7 — 2$; this optimum coincides with that observed with dissolved protein, although, if the swelling had any influence, displacement of the optimum would be expected. Further experiments show that the whole course of the digestion curve, as well as the position of the optimum, may be attributed solely to the concentration of the hydrogen ions by virtue of their simultaneous actions on the protein and on the pepsin. The position of the optimal hydrogen-ion concentration is never affected by the nature of the anion of

the acid, but this may in some cases, for instance, with sulph salicylic acid, influence the absolute amount of digestion.

T. H. P.

The Significance of Gastric Hydrochloric Acid, and th Importance of the H-ion Concentration in Biologic Sciences. I. TRAUBE (*Biochem. Zeitsch.*, 1920, **107**, 295—29 —A theoretical paper.

S. S. Z.

The Problem of Nuclein Metabolism. The Formatio of Uric Acid after Parenteral Administration of Purin Nucleosides in Healthy Men. JULIUS ROTHER (*Zeitsch. physio Chem.*, 1920, **110**, 245—253).—A rise was observed in the ur acid excretion of patients who previously received an intramuscul injection of guanosine. The author points out that, as the treate patient manifested high temperatures and other abnorm symptoms, it is possible that the increase in the uric acid may no have been due entirely to the decomposition of the guanosine, bu may have been produced endogenously, owing to the disturbe condition of the patient.

S. S. Z.

Intermediate Metabolism and its Active Enzymes TORSTEN THUNBERG (*Skand. Arch. Physiol.*, 1920, **40**, 1—91; fro *Chem. Zentr.*, 1920, iii, 390—391).—The severed muscular tissu of a recently killed frog, after being extracted with water, lose the power of decolorising methylene-blue in a medium free fro oxygen; this capacity can, however, be restored by the additio of certain substances, since, under the action of an enzyme, tw atoms of hydrogen are removed from the latter and transferred t the dye, with consequent formation of its leuco-base. The cell are provided with an enzyme which is specifically active toward those substances which activate the decolorising capacity, and thes substances therefore probably represent intermediate stage through which the primary simple nutrient materials pass in the transformation into the final products. The author therefore con siders materials such as dextrose, fats, amino-acids, etc., to underg a series of transformations by indirect oxidation effected b "dehydrogenation." The newly discovered enzymes, in thei capacity as "hydrogen transportases," bring about the removal c hydrogen from the nutrient material, which either combines wit oxygen or is employed in the halogenation of other substance According to this conception, all nutrient material, no matter c how diverse a character, must be able to yield hydrogen. Th latter is the universal fuel for all cells. The replaceability of on food by another is therefore regarded in a new light.

The following substances act as powerful restorers of the los decolorising power: formic, acetic, butyric, hexoic, succini fumaric, maleic, tartronic, *l*- and *dl*-malic, *l*-, *r*-, and *meso*-tartari *l*-*α*-hydroxyglutaric, citric, lactic, *α*- and *β*-hydroxybutyric, pyruvi and glutamic acids, and alanine. On the other hand, the followin materials are inactive: propionic, *iso*butyric, *iso*valeric, crotonic allylacetic, oxalic, malonic, glycollic, hydroxy*iso*butyric, methyl

succinic, glutaric, adipic, and a number of other saturated and unsaturated dicarboxylic acids, glycine, leucine, phenylalanine, and other amino-acids, creatine, creatinine, guanidine hydrochloride, taurine, urea, and glucosamine.

It is possible to differentiate between the various enzymes from the mixture in the muscle by powerful and rapid cooling and by increase in temperature; the enzymes which act on the different acids mentioned above show a very uneven resistance to alterations in temperature and a pronounced "cryolability." H. W.

The Relation of Cholesterol to the Intermediate Stage of Fat Metabolism. W. HUECK and L. WACKER (*Biochem. Zeitsch.*, 1919, **100**, 84—99).—The free and esterified cholesterols were estimated in the total blood, the serum, and in the fresh and dried erythrocytes and leucocytes in the blood of various animals. The results are given in a table. The erythrocytes are characterised by the absence of cholesterol esters. The cholesterol in animal fat was found to be present mostly, if not entirely, as free cholesterol. Cholesterol was also fed to rabbits, and the lipoid fraction of the blood was examined in these animals as well as in normal and starving rabbits. The results show a great variation in the cholesterol content of the blood of normal rabbits. An increase was found in the total lipoids, the free and esterified cholesterol, and the lecithin in the blood of the animals which received the cholesterol. Lipæmia was observed in the starved animal. S. S. Z.

Action of the Accessory Food Factors. FRITZ VERZÁR and JOSEF BÖGEL (*Biochem. Zeitsch.*, 1920, **108**, 185—206).—The pharmacological action of extracts of the fat-soluble *A* and water-soluble *B* accessory food factors on various organs was examined. No characteristic behaviour of these factors could be established. S. S. Z.

Amino-acids in Nutrition. I. Studies on Proline: Is Proline a Growth-limiting Factor in Arachin (Globulin from the Pea-nut)? BARNETT SURE (*J. Biol. Chem.*, 1920, **43**, 443—456).—The biological value of arachin as tested on rats appears to be low, but the low content of proline is not the factor limiting growth. Evidence in support of this is given by experiments, which showed that proteins rich in proline, such as zein and gelatin, do not supplement the protein arachin. Other experiments show that the low nutritive value of arachin is not raised by additions of tryptophan, cystine, a mixture of glycine, alanine, and valine, or by the sister globulin, conarachin.

Lactalbumin supplements arachin, particularly when cystine is also added. J. C. D.

Amino-acids in Nutrition. II. The Nutritive Value of Lactalbumin: Cystine and Tyrosine as Growth-limiting Factors in that Protein. BARNETT SURE (*J. Biol. Chem.*, 1920, **43**, 457—468).—The proteins removed from milk by coagulation,

after caseinogen has been separated, do not possess a high biological value for growth in rats. Cystine and tyrosine will raise this value and supplement the protein deficiencies. Lactalbumin is not, however, a protein with an unusually low cystine content, and this suggests that the efficiency of a protein may largely depend on its constitution as well as on its composition of amino-acids. The author suggests that the opinion expressed by Osborne and Mendel (A., 1916, i, 690), that lactalbumin is a protein of high nutritive value, is founded on experiments which are open to criticism. Evidence was obtained that organically-bound sulphur and a substance giving a Millon reaction are present to an appreciable extent in protein-free milk. J. C. D.

Capillarisation in Biochemistry. RUDOLF KELLER (*Biochem. Zeitsch.*, 1920, **107**, 43—49).—A theoretical paper on capillary electricity. S. S. Z.

Taste. SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1920, **41**, 495—534).—Considering the facts that (1) optical isomerides have different taste, (2) substitutions always affect the taste, (3) all the compounds containing either Cohn's sapophore group or Oertly and Meyer's glucophore contain vibratory hydrogen, and (4) the taste of electrolytes is due to the sum of the tastes of molecular electrolyte, anions, cations, and complex ions, the author proposes a theory that the taste of organic substances is due to electric vibration of the sapophoric element. A detailed explanation, and examples with several hnndreds of different compounds, are given. Applications of the theory in physiology, psychology, and medicine are suggested. Methods of preparation of different optical isomerides used for taste experiments are included in the last chapter. CHEMICAL ABSTRACTS.

Taste. YRJÖ RENQVIST (*Skand. Arch. Physiol.*, 1918, **38**, 97—201; from *Chem. Zentr.*, 1920, i, 591).—The taste system is composed of the sensory particles and their components and the liquid or solution; it is thus a heterogeneous system, one part of which comprises the colloidal protoplasmic taste cells or nerve terminations, and the other the liquid or solution. The main changes which occur depend on alteration of surface and electrical energy. Equally marked sensations of taste must correspond with the adsorption of equal amounts of the substance by the organs of taste. The concentration necessary to induce taste with the alkali salts is an additive function of the inverse values of the rates of migration of the ions. The concentration for barium and calcium chlorides is less than that for the alkali salts, whilst for aluminium chloride a minimum value is attained. Valency is therefore an important factor, and this appears to indicate a suspensoid character of the adsorption in the system of taste. In addition to the rate of adsorption, electrical phenomena are also important in their effect on the induction of taste by different electrolytes. The phenomena of the sensation of taste produced by homologous and isomeric compounds are explicable on the

assumption that the process is one of adsorption. Experimental investigation confirms the accuracy of a deduction, from which it appears that the sensation of taste is more persistent with increasing concentration of tasted substance and increasing adsorption exponent, and with decreasing inducing concentration and rate of diffusion. The author also examines the qualities of taste, their variation with differing concentrations of electrolyte, and their relationships to the differences of potential caused by the electrolyte in the sensory system. The quality of the induced taste can be foretold with some degree of accuracy if the rate of migration of the ions of a univalent electrolyte and its concentration are known. The "compensation of taste" is a peripheral phenomenon which is observed in the sensory system; a bitter taste is not however, compensated. The "fundamental tastes," sweet, bitter and sour, are chosen, from which, in analogy to the Young-Helmholtz theory of colour vision, all the various sensations of taste can be compounded. H. W.

The Inducing Value of the Sensation of Taste by certain Homologous and Isomeric Compounds. YRJÖ RENQVIST (*Skand. Arch. Physiol.*, 1920, **40**, 117—124; from *Chem. Zentr.* 1920, iii, 425—426).—The concentrations requisite to produce the sensation of taste have been estimated for six different alkyl esters of cyanoacetic acid, the methyl and ethyl esters of oxalic, malonic and succinic acids, the homologous monohydroxy-alcohols from methyl to octyl alcohol, and various isomeric esters of certain ethe acids. In the majority of cases, the results are in agreement with the relationships established previously (preceding abstract between the inducing concentration for taste and the coefficient of diffusion. The inducing concentrations of isomerides are approximately equal, whilst with homologous compounds they diminish with increasing molecular weight. The surface tension of isomeric substances at the inducing concentration are determined by the drop method, and found to be approximately equal. H. W.

Protamine from the Spermatozoa of the Japanese Mackerel, Scomber japonicus. KUNIHIKO SUMIKURA (*J. Tokyo Chem. Soc.*, 1920, **41**, 281—310).—Crude protamine is prepared by Kossel's method, dissolved in hot water, histone is removed by precipitation with ammonia, and the filtrate is neutralised with sulphuric acid. By adding a nentralised sodium tungstate solution, a white precipitate is obtained, which is recrystallised repeatedly and dried over sulphuric acid. This product is redissolved in hot water, and ½ vol. of 50% alcohol is added to obtain a white turbidity. Cooling over ice and the addition of ether give the oily substance, which, after being washed seven to eight times with water saturated with ether, is precipitated by alcohol (three times the original vol.). The precipitate is washed with alcohol–ether mixture and dried over sulphuric acid. Such protamine contains 20·31% N, 7·15% H, 36·48% C, 22·03% H_2SO_4, corresponding wit

$C_{30}H_{71}O_9N_{14},2H_2SO_4$, which shows less nitrogen, and more hydrogen and oxygen, than scombrin, prepared from European mackerel by Kurajev. Hydrolysis gives 0·609% of ammonia-nitrogen, 0·096% of hexone base nitrogen, 71·73% of arginine nitrogen, 17·26% of monoamino-nitrogen, on the basis of 100 parts of the total nitrogen. Lysine is absent, and the presence of histidine is doubtful. The protamines of European and Japanese mackerels are probably not identical. CHEMICAL ABSTRACTS.

Proteinogenous Amines. X. The Response of the Excised Uterus to Potassium, Rubidium, and Cæsium Ions. MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, **43**, 579—582).—Potassium and rubidium salts in concentrations of about *N*/75 produce tonic contraction of the virgin uterus of the guinea-pig, from which the muscle does not recover until the stimulating ions are removed.

The response with cæsium is less marked. J. C. D.

Lipoids. XVII. Dilignoceryl-*N*-diglucosamine Monophosphoric Ester, a New *Diaminomonophosphatide* from the Brain. S. FRÄNKEL and F. KAFKA (*Biochem. Zeitsch.*, 1920, **101**, 159—171. Compare A., 1914, i, 128).—Brain dried in a vacuum at a low temperature, and freed from cholesterol by extraction with acetone, was extracted with boiling light petroleum. The concentrated petroleum fraction was extracted further with absolute alcohol. A lead compound, $C_{60}H_{111}O_{14}N_2PPb_3$, decomposition point 305—308°, was obtained from this fraction, which, unlike Thudichum's myelin, was soluble in ether. It was also soluble in benzene, but not in alcohol. By decomposing the lead salt with hydrogen sulphide, the free compound, $C_{60}H_{117}O_{14}N_2P$, m. p. 190°, was obtained. On hydrolysis, lignoceric acid, glucosamine, and phosphoric acid were obtained from this compound. It is, therefore, *dilignoceryl*-N-*diglucosamine monophosphoric ester*.

S. S. Z.

Unsaturated Lipoids of the Liver. P. A. LEVENE and T. INGVALDSEN (*J. Biol. Chem.*, 1920, **43**, 359—378).—The unsatisfactory state of the knowledge regarding the phosphatides of the liver led the authors to reinvestigate the subject. The unsaturated lipoids of other organs have been classified as (1) acetone-soluble lipoids, consisting principally of lecithin with small proportions of cephalin; (2) acetone-insoluble, but alcohol-soluble, fraction, which consists of lecithin with larger proportions of cephalin; and (3) a fraction insoluble in acetone and alcohol, which consists of very small proportions of lecithin with larger amounts of cephalin, together with substances which are derived from the lipoids themselves.

These three fractions, with their general characteristics, were obtained from liver tissue, and in this respect the lipoid material obtained from the liver is similar to that obtained from the other organs. A study of the lecithin isolated from the liver reveals that there are two fatty acids in the molecule, one saturated, stearic

cid, and the other unsaturated and of the linolic series. No vidence of the presence of oleic acid was obtained.

The paper records progress in the attempts to prepare a pure pecimen of cephalin. Preparations containing 70% have been btained.

J. C. D.

Presence of a Large Amount of Cholesterol Ester in the iver Oil of the Basking-shark, Cetorhinus maximus, unner. MITSUMARU TSUJIMOTO (*Bull. Tokyo Ind. Research Lab.*, 920, **15**, No. 2, 1—10).—So far, an animal oil has never been eported to contain more than 3% of cholesterol. The oil extracted t 100° from the liver of a young basking-shark had D^{15} 0·9176, cid number 0·301, saponification number 14·57, Wijs number 74·4, n^{20} 1·4836, butyrorefractometer at 20°, 87·2, [α] −2·7, unaponifiable matter 20·55%. It contained 9% of squalene. 42% f the unsaponifiable substance is found to be cholesterol ester, orresponding with 8·6% of original oil. More than 90% of the holesterol exists as ester, the remainder being free. By means of pase, this cholesterol ester was separated from other fat. Whether the presence of such a large amount of cholesterol in the il of this shark is characteristic of this fish or is due to a peculiar athological condition which might be associated with this articular specimen has not been yet determined.

CHEMICAL ABSTRACTS.

The Monoamino-acids of the Lens of the Eye. A. JESS *Zeitsch. physiol. Chem.*, 1920, **110**, 266—276).—The monoaminocid content of the albumoid, the α-cristallin, and the β-cristallin f the lens of the eye has been determined. The outstanding eature of this analysis is that the alanine content of the albumoid low, 0·8% against 2·6% and 3·6% in the β-crystallin and the crystallin respectively. Only traces of valine (0·2%) could be etected in the albumoid. One-half of leucine and its isomerides ould be established in the β-crystallin as compared with the uantities of these substances present in the α-crystallin and the bumoid. No very striking differences in the content of the other onoamino-acids of these proteins could be established. S. S. Z.

The Capacity of the Animal Skin to React with Phenolldehydes. OTTO GERNGROSS (*Biochem. Zeitsch.*, 1920, **108**, 2—97).—Glycylglycine ester when treated with *o*-protocatechuldehyde and *o*-vanillin, respectively, yields compounds showing golden-yellow colour similar to that obtained when skins are eated with these substances. A combination of *o*-protocatechuldehyde with *l*-tyrosine methyl ester yielded a similar colour. Hide powder previously treated with formaldehyde was only slightly oloured by phenolaldehydes, and this colour could be washed out. his shows that the basic groups of the skin react with the phenolldehydes in the ordinary way. On the other hand, treated and ntreated skins gave the same coloration with sodium diazobenzeneulphonate. The imino-group of the iminazole ring does, therefore, ot react with formaldehyde. *o*-Protocatechualdehyde is capable

tanning skins, *o*-vanillin is not. The author attributes the .nning action to the two hydroxyl groups in the benzene ring of ie former compound. He also suggests the possibility that the louring action of the phenolaldehydes is not dne to the aldehyde, it to the phenol group. The colouring cannot be ascribed to the rmation of a Schiff's base. S. S. Z.

Amino-acids of the Blood as the Precursors of Milk roteins. C. A. Cary (*J. Biol. Chem.*, 1920, **43**, 477—489).—In ie non-lactating cow, the level of amino-acid nitrogen is approxim-ely the same in the blood from the mammary vein and from the igular vein. When the mammary gland is active, however, the vel of amino-acid nitrogen is very much lower in the blood in ie mammary vein than in the jugular. This indicates that the oteins of the milk are built up from amino-acids brought to the and by the arterial system.

The carbon dioxide capacity of the plasma has also been studied both conditions, but the significance of the results is uncertain.

J. C. D.

Influence of Ether or Alcohol on the Coagulation of ilk. Influence of Sodium Nucleinate on the Coagulation Milk and Blood. M. Doyon (*Compt. rend. Soc. Biol.*, 1920, **83**, 8—919; from *Chem. Zentr.*, 1920, iii, 395).—The coagulation of ilk by rennet is noticeably facilitated by the presence of ether alcohol, but retarded by sodium nucleinate; the latter effect is mediately removed by addition of calcium chloride. Blood es not coagulate, but rapidly suffers very marked hæmolysis when ought directly into sodium nucleinate; in this case, also, agulation is immediately induced by the addition of calcium loride. H. W.

The Technique of Urine Acidimetry (specially for inical Purposes). W. Biehler (*Zeitsch. physiol. Chem.*, 1920, **.0**, 298—306).—The H-ion concentration of urine calculated om titration figures differs from values obtained by direct estim-ion of the H-ion concentration. By plotting curves from the lues obtained by the two methods, it is seen that there is a ationship between the two sets of results. It is suggested that e real H-ion concentration can be obtained by titration and mparing the two curves. S. S. Z.

Pyrrole and Melanuria. III. Pietro Saccardi (*Gazzetta*, 20, **50**, ii. 118—128. Compare A., 1919, i, 421; this vol., 203).—In view of the fact that by some tyrosine and by others renaline is regarded as the mother substance of the melanins, e author has made experiments the results of which indicate at tyrosine alone is not capable of giving rise to melanin, since exhibits great resistance to organic and inorganic oxidising ents; adrenaline is considerably more sensitive than tyrosine to idising agents, and, under the action of chlorine water, yields a own precipitate of the appearance of melanin.

Pyrrole administered by ingestion is slowly absorbed and slowly eliminated by man, and large doses are necessary to produce melanuria, since the organism partly destroys it and partly eliminates it unchanged; when injected, pyrrole is largely oxidised.

Egg-albumin, but not dextrose, yields a true melanoidal substance when subjected to protracted boiling with concentrated hydrochloric acid.

Melanins from hair, from the choroid, and from a melanotic tumour undergo vigorous oxidation when treated with peracetic acids, and yield minute, acicular or tabular crystals, which, in view of the resemblance between the phenomena of these oxidations and those of the oxidation of pyrrole-black, may consist of succinic acid or succinimide. T. H. P.

The Physiological Action of Silicic Acid. The Influence of Silicic Acid on the Animal Organism. FRANZ SCHUHBAUER (*Biochem. Zeitsch.*, 1920, **108**, 304—308).—Merck's preparation of natrium silicium purissimum is hydrolysed in the intestine by the action of water, with the formation of sodium hydroxide. This change can be obviated by neutralising the preparation.

S. S. Z.

The Physiological Action of Silicic Acid. The Absorption of Silicic Acid. FR. BREEST (*Biochem. Zeitsch.*, 1920, **108**, 309—316).—A rise in the silica content of the body can be established by increasing the silica in the food in a suitable form. Only a small portion of the administered silica is retained by the body. The author confirms Schuhbauer's results concerning the hydrolysis of Merck's silicates (see preceding abstract). S. S. Z.

Do Amino-acids Possess Secretin Characteristics? SCHWEITZER (*Biochem. Zeitsch.*, 1920, **107**, 256—267).—Amino-acids obtained by hydrolysis of protein with hydrochloric acid at 100° have shown no definite secretin action on the gastric glands. It is concluded from some of the experiments that secretin activity is not due to a single definite chemical substance, but may be produced by various compounds. S. S. Z.

The Physical Theory of Pharmacological Actions. WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1919, **101**, 54—61).—A theoretical paper in reply to Traube (this vol., i, 204).

S. S. Z.

Pharmacological Actions of the Reduction Products of Coumarin. K. FROMHERZ (*Biochem. Zeitsch.*, 1920, **105**, 141—144. Compare Ellinger, A., 1908, ii, 1060; Trendelenburg, *Arch. exp. Path. Pharm.*, 1915, **79**, 9, 190).—The author has investigated the action on various animals of hydrocoumaric acid, its lactone (melilotol), *o*-hydroxyphenylpropyl alcohol, and the ether of this alcohol (chroman). The results obtained show that, with the exception of hydrocoumaric acid, these compounds exhibit approximately the narcotic properties of coumarin, but show no

advantages, especially as regards the ratio of toxicity to activity over the parent substance. Further, Fränkel's view ("Arzneimittelsynthese"), that coumarin is a substance which exert narcotic effects in virtue of its carbonyl group, is contradicted since reduction of the carbonyl to methylene does not remove th narcotic properties. Comparison of hydrocoumaric acid wit melilotol appears to indicate that the lactone ring is of significanc as regards narcotic action, but this indication fails when the lowe stages of the reduction are reached. T. H. P.

Quantitative Studies in Chemotherapy. I. The Trypanocidal Action of Antimony Compounds. CARL VOEGTLI and HOMER W. SMITH [with MARIAN M. CRANE, KATHERINE D WRIGHT, and MABEL A. CONNELL] (*J. Pharm. Exp. Ther.* 1920, **15**, 453—473).—The specific action of antimony lactate ca be studied fairly accurately by following the disappearance of th *trypanosomes from the blood stream of infected rats. There is* a sharply defined threshold stage, below which the drug has no appreciable effect on the parasites. The process curve is an orderly one, and consistent throughout individual experiments.

J. C. D.

Quantitative Studies in Chemotherapy. II. The Trypanocidal Action of Arsenic Compounds. CARL VOEGTLIN and HOMER W. SMITH [with MARIAN M. CRANE, KATHERINE D. WRIGHT, and MABEL A. CONNELL] (*J. Pharm. Exp. Ther.*, *1920*, **15**, *475—493*).—Differences in the toxicity of various arsenic preparations have been explained on the hypothesis that they must be changed into one type, namely, the tervalent oxides. RAs:O, before exerting their principal toxic effect. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Metabolic Action of Bacteria. FRITZ VERZÁR and JOSEF BÖGEL (*Biochem. Zeitsch.*, 1920, **108**, 207—219).—*Streptococcus haemolyticus* forms only acid, but not alkali, with dextrose. The acidity attained by *Bacillus paratyphosus*-B and *B. proteus* is independent of the initial reaction. In the formation of acid, *B. coli communis* produces gas; on the other hand, it uses up oxygen when it forms alkali. There is no connexion between mobility and gas formation in paratyphoid organisms. Ethyl alcohol, methyl alcohol, chloroform, and formaldehyde inhibit the gas exchange of these organisms. Much smaller doses produce definite retardation. A relation between the maximum acid formation and the presence of alcohols is established. S. S. Z.

The Chemical Composition of the Tubercle Bacillus. A. Goris (*Ann. Inst. Pasteur*, 1920, **34**, 497—546).—See this vol., i, 582.

Antagonistic Action of Calcium and Iron Salts toward other Salts as measured by Ammonification and Nitrification. J. E. Greaves (*Soil Sci.*, 1920, **10**, 77—102).—Experiments were made on the effect produced on the bacterial activity of a fertile, sandy loam soil by the addition of calcium and iron salts. The ammonifying and nitrifying powers of the soil were first reduced by the addition of various salts, then increasing amounts of the calcium salt or the iron salt were added, and the effect on ammonification and nitrification was observed. Calcium sulphate was found to neutralise the toxic effect on ammonification of sodium carbonate, nitrate, and sulphate, calcium chloride, and magnesium chloride and sulphate. It had no antagonism to sodium chloride. Similar results were obtained in the case of nitrification, except that there was no antagonism towards sodium sulphate and calcium chloride. Thus both the anion and cation take part in the antagonism.

Ferrous sulphate was found to be antagonistic to sodium sulphate, chloride, carbonate and nitrate, and calcium chloride; ferrous chloride to sodium chloride and nitrate, calcium chloride, and magnesium sulphate; ferrous nitrate to magnesium chloride and sulphate, calcium chloride, and sodium carbonate, sulphate, chloride, and nitrate; ferrous carbonate to sodium chloride and carbonate, calcium chloride, and magnesium sulphate. The greatest effect was produced by ferrous carbonate on magnesium sulphate, in which mixture 75% of the toxic effect was neutralised. In the case of nitrification, the order differed, and the greatest effect was produced by ferrous nitrate against magnesium chloride. The quantity of iron required for maximum effect varied with the different salts, but in no case exceeded 186 parts per million.

J. H. J.

The Pharmacology of Selenium and Tellurium. I. The Action of their Acids on Bacteria. Georg Joachimoglu (*Biochem. Zeitsch.*, 1920, **107**, 300—312).—The ions of tellurous and selenious acids are much more active than those of telluric and selenic acids. The growth of moulds is scarcely affected by the action of tellurites and tellurates. Bacteria, especially of the typhus-coli group, are, on the other hand, very sensitive to the action of these substances. The author suggests the application of tellurium compounds in the chemotherapy of typhoid infection.

S. S. Z.

Oligodynamy of Silver. R. Doerr (*Biochem. Zeitsch.*, 1920, **106**, 110—133).—"Oligodynamic" water, that is, water which by prolonged contact with metallic silver has become bactericidal, shows all the properties of an antiseptic. Dilution with distilled water or concentration by distillation produces the corresponding

quantitative change, but no qualitative change, in the antiseptic power; the distillate acquires no such property. If reducing substances are excluded, boiling causes no diminution in the bactericidal action of the water. The presence of sodium chloride retards this action, and that of horse serum destroys it. The antiseptic property of oligodynamic water appears to be to some extent specific, bacteria of different species exhibiting resistance in different degrees. Solutions of definite silver compounds show the same properties as oligodynamic water. T. H. P.

Oligodynamics of Silver. II. R. DOERR (*Biochem. Zeitsch.*, 1920, **107**, 207—218).—The bactericidal action of metallic silver disappears when the metal is ignited, boiled several times in distilled water, or is embedded in an agar jelly. The inactivated metal can be reactivated by being treated with very dilute solutions of a strongly dissociated acid. The oligodynamic principle of silver is dialysable, and shows the same properties of diffusion in agar jellies as silver oxide and silver nitrate. Bacteria seeded on an agar plate containing metallic silver, silver oxide, or silver nitrate grow often in two concentric rings similar to the Liesegang phenomenon. Pieces of silver embedded in a blood-agar plate produce hæmolytic zones. S. S. Z.

The Antiseptic Action of Some Chlorine Derivatives of Methane, Ethane, and Ethylene. E. SALKOWSKI (*Biochem. Zeitsch.*, 1920, **107**, 191—201).—The suitability as preservatives of methyl chloride, chloroform, methylene chloride, acetylene dichloride, trichloroethylene, and ethyl chloride was tested. Trichloroethylene, on account of its low price, of the small quantities required to be employed, and of its volatile character, was found to be the most suitable preparation. S. S. Z.

Dependence of Yeast-growth and Fermentation on Physico-chemical Phenomena. FRIEDRICH BOAS (*Biochem. Zeitsch.*, 1920, **105**, 193—198).—The author's experiments on the fermentation of dextrose solutions containing different proportions of ammonium sulphate confirm the observation that fermentation exhibits an optimum for a definite concentration of nitrogenous material. The results obtained by Pringsheim (A., 1907, ii, 287; 1908, ii, 316) with asparagine and ammonium sulphate are considered in the light of colloidal chemistry, and the conclusion is drawn that the plasma membrane of the yeast cell, somewhat in the same way as a lecithin membrane, is rendered either denser or looser by different concentrations of nitrogenous substances, the sugar thus entering the yeast cell either slowly or rapidly, and the fermentation being correspondingly slow or rapid. When peptone is used as source of nitrogen, maxima of fermentation similar to those obtained with asparagine, etc., are observed at first, the peptone being thus converted into crystalloid nitrogen compounds at the plasma membrane; this phenomenon soon disappears, owing, presumably, to the formation from the peptone of compounds which

counteract the crystalloid compounds. These membrane effects are observed also with synthetic leucine, but not with natural leucine derived from molasses. T. H. P.

Rhythmic Phenomena in the Growth and Fermentation of Yeast. ERICH KÖHLER (*Biochem. Zeitsch.*, 1920, **106**, 194—206).—The processes of fermentation and of multiplication of yeast are found to exhibit a certain periodicity, which is caused by alterations in the sugar and alcohol contents of the nutrient solution. The velocity with which the yeast grows is conditioned by the concentration of the sugar, and varies irregularly as this concentration increases. T. H. P.

Course of Alcoholic Fermentation by Yeast. ERICH KÖHLER (*Biochem. Zeitsch.*, 1920, **108**, 235—243).—The course of alcoholic fermentation by yeast becomes rhythmic with the increase in the concentration of the alcohol. S. S. Z.

Formation of Acid with Moulds and Yeasts. IV. FRIEDRICH BOAS, HANS LANGKAMMERER, and HANS LEBERLE (*Biochem. Zeitsch.*, 1920, **105**, 199—219. Compare A., 1919, i, 508).—The results of further experiments with yeasts indicate that different sugars act to different extents on the plasmic membrane, so that they may be arranged in order of diminishing utilisability by yeasts, as follows: maltose, dextrose, lævulose, sucrose. With many yeasts, this action on the membrane is zero with maltose and very considerable with sucrose. Such specific action of the sugars may be more or less altered, but not obliterated, by acclimatisation. Further, from the results obtained by other investigators, it appears that alteration in the reaction of the liquid and in the concentration of the nitrogenous substances may effect slight displacements in the above series of sugars. With a maltose solution containing ammonium chloride, the maximal acidity reached during fermentation was $p_H = 2{\cdot}55$, and with a whortleberry juice containing sucrose and ammonium chloride, the value $p_H = 1{\cdot}85$ was reached on brisk fermentation (compare Euler and Heintze, this vol., i, 513). T. H. P.

Maltase Solutions from Yeast. R. WILLSTÄTTER, TH. OPPENHEIMER, and W. STEIBELT (*Zeitsch. physiol. Chem.*, 1920, **110**, 232—240).—Maltase can be obtained from fresh beer yeast previously killed by an antiseptic, such as chloroform or toluene, by extracting it with water in the presence of ammonia. The authors suggest that, owing to some enzymic process, acid is formed in the yeast cell, which is responsible for the destruction of the maltase when it is extracted from the undried cell, and that the neutralising effect of the ammonia makes it therefore possible to obtain the enzyme also from the fresh yeast cell. The relation between the concentration of the enzyme and the decomposition of the maltose, as well as the velocity of the reaction, was studied

with maltase preparations from dried and fresh yeasts. The activity of maltase solutions is impaired by treatment with kaolin.
S. S. Z.

The Influence of Surface-active Nonoic Acid and of Some Surface Active Homologues of the Alcohol Series (Amyl Alcohol and Octyl Alcohol) on the Yeast Cell and on Fermentation. WILHELM WINDISCH, WILHELM HENNEBERG, and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1920, **107**, 172—190). —0·005—0·02% of nonoic acid has an inhibitive action on yeast fermentation. 0·017—0·04% of octyl alcohol has a similar effect. Higher concentrations of amyl alcohol are required to produce inhibition in fermentation. Nonoic acid and octyl alcohol also produce a diseased condition of the yeast cell, altering its appearance with the production of fat in the cell. The experiments point to the fact that the action of these substances is not due to their chemical properties, but to their surface action. S. S. Z.

Physico-chemical Considerations in connexion with Neuberg's Theory of Fermentation. WOLFGANG OSTWALD (*Biochem. Zeitsch.*, 1919, **100**, 279—288); CARL NEUBERG (*ibid.*, 289—303).—A suggestion is put forward by Ostwald that physical factors, such as adsorption, might exercise some influence in the fixation of intermediate products of fermentation, such as acetaldehyde. To this Neuberg replies. S. S. Z.

The Relation of Aldehydes to Alcoholic Fermentation. CARL NEUBERG and MARTA EHRLICH (*Biochem. Zeitsch.*, 1920, **101**, 239—277. Compare A., 1918, i, 469).—The influence of seventy-one aldehydes on alcoholic fermentation was tested. It was found that the stimulating effect of the aldehyde group was general and independent of the radicle associated with it. This activation takes place whether the fermentation is produced by the living yeast or by the cell-free juice. S. S. Z.

The Relation of Phytochemically Reducible Substances to the Process of Alcoholic Fermentation and the Nature of the Action of Activators. CARL NEUBERG and MARTA EHRLICH (*Biochem. Zeitsch.*, 1920, **101**, 276—318. Compare preceding abstract).—Numerous experiments are described which show that most ketones and their derivatives and phytochemically reducible substances are capable of activating alcoholic fermentation. This activating influence is not so marked, in fact, almost absent, with the lower ketones. S. S. Z.

So-called Methyl-alcoholic Fermentation. EDMUND O. VON LIPPMANN (*Biochem. Zeitsch.*, 1920, **106**, 236—238).—Examination of twenty samples of genuine rums confirms the observation that such spirits often contain methyl alcohol in considerable proportion, as much as 7·5—8·5% of this alcohol being found in three of the samples. Much of the extraction of sugar

cane in the Lesser Antilles is carried out in *presses*, and the juice is subjected to inadequate clarification and mechanical purification, so that it contains considerable proportions of very fine cane fibre, which passes to a large extent into the syrups and molasses. This fibre is rich in pectinous material, and as the pectins consist of the methyl ester of pectinic acid and are readily decomposed in various ways, with liberation of methyl alcohol, the origin of the latter is evident. T. H. P.

Production of Gas during the Acetone and Butyl Alcohol Fermentation of Starch. HORACE B. SPEAKMAN (*J. Biol. Chem.*, 1920, **43**, 401—411).—From a study of the production of gas during this fermentation, a scheme is suggested to account for the substances formed which is believed to be in harmony with experimental observations, the requirements of the organism, and the conditions during fermentation.

It has been previously shown that the first two stages of the fermentation may be represented by the equations

$$(1)\ \underset{\text{Starch.}}{(C_6H_{10}O_5)_x} + xH_2O = \underset{\text{Dextrose.}}{xC_6H_{12}O_6}$$

$$(2)\ \underset{\text{Dextrose.}}{C_6H_{12}O_6} = \underset{\text{Butyric acid.}}{C_3H_7\cdot CO_2H} + \underset{\text{Acetic acid.}}{CH_3\cdot CO_2H} + [O_2]$$

The oxygen produced during the second reaction cannot be detected by ordinary chemical methods, and must therefore be used up in associated reactions, in which oxidation plays a part. Now, production of acetone commences very early in the fermentation and before the appearance of the butyl alcohol, whilst the gas given off at the commencement is pure hydrogen, but later a gradual and increasing dilution with carbon dioxide occurs. From this evidence it may be concluded that a later stage of the fermentation may be represented by the equations:

$$(3)\ \underset{\text{Butyric acid.}}{2C_3H_7\cdot CO_2H} + O_2 = \underset{\text{Acetoacetic acid.}}{2CH_3\cdot CO\cdot CH_2\cdot CO_2H} + 2H_2$$

$$(4)\ CH_3\cdot CO\cdot CH_2\cdot CO_2H = \underset{\text{Acetone.}}{CH_3\cdot CO\cdot CH_3} + CO_2$$

The intermediate formation of acetoacetic acid has not been proved experimentally, but Raistrick and Clark (this vol., i, 352) have already suggested that it occurs.

The formation of butyl alcohol, and to a much smaller degree of ethyl alcohol, takes place by the reduction of the corresponding acid:

$$(5)\ C_3H_7\cdot CO_2H + 2H_2 = CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + H_2O.$$
$$(6)\ CH_3\cdot CO_2H + 2H_2 = CH_3\cdot CH_2\cdot OH + H_2O.$$

Other points require further study, as, for example, the disappearance of a larger amount of acetic acid than can be accounted for by the amount of ethyl alcohol produced, the volume of

hydrogen and carbon dioxide given off, which cannot be accoun for by the activity of reactions previously mentioned in t scheme, and the consumption of oxygen made available by production of butyric acid, which is not oxidised to acetone, l reduced to alcohol. J. C. D

The Third Form of Fermentation of Sugar. CARL NEUB and JULIUS HIRSCH (*Biochem. Zeitsch.*, 1919, **100**, 304—322) In the presence of alkaline salts, sugar, when fermented by yea undergoes a cleavage into acetic acid, ethyl alcohol, carbon dioxi aud glycerol. This abnormal fermentation the authors call "third form of fermentation," in contradistinctiou to the norr process and the process of fermentation carried out by fixing t acetaldehyde produced with an agent, such as sodium sulphite "the second form of fermentatiou." Fermentation of sugar by ye in the presence of potassium carbonate, dipotassium phospha magnesium oxide, trisodium phosphate, disodium phosphate, and "buffer mixture" of monosodium and disodium phosphate, yield products of fermentation characteristic of the "third form fermentation." In the presence of aluminium hydroxide a colloidal iron hydroxide, the fermentation was normal. Duri fermentation of sugar in molar dipotassium phosphate, a sixfo production of acetaldehyde is observed in the early stages of t fermentation This falls to the normal rate as fermentati proceeds. S. S. Z.

The Gaseous Exchanges of the Root with the Atmosphere. RAOUL CENGHELLI (*Compt. rend.*, 1920, **171**, 575—578). In a confined atmosphere, plant roots respire in much the sar way as other organs, the ratio of carbon dioxide expired to oxyg inspired varying from 0·7 to 1, according to the species. In very moist atmosphere there is an increase in the rate of respir tion, but the above ratio remains constant. When the roots a in contact with a very moist atmosphere and still attached to t aerial organs, there is further increase in the respiration, but t carbon dioxide formed is not completely expired, so that t respiratory-coefficient is low. W. G.

The Velocity of the Photochemical Degradation of Carbon Dioxide in Living Cells. OTTO WARBURG (*Biochem. Zeitsch.*, 1919, **100**, 230—270. Compare this vol., i, 583).—Th velocity of assimilation of carbon dioxide is proportional to th concentration of the gas when the concentration is low. Wit higher concentrations, the velocity of assimilation increases pro portionately less as the concentration of the carbon dioxid increases until it is no more influenced by the concentration. I the case of illuminations of low intensity, the velocity of assimi ation is also proportional to the intensity of the illumination, bu with higher illuminations the increase in the velocity of assimilatio becomes lower as the intensity of the illumination increase

Temperature influences the assimilation of carbon dioxide in high concentrations of the gas when intensely illuminated in a pronounced degree. Between 5° and 32°, the temperature-coefficient sinks from 4·3 to 1·6. In the case of illuminations of high intensity, more carbon dioxide is decomposed by the same quantity of energy when the illumination is intermittent than when it is continuous. This differentiation does not take place when the illumination is low. The influence of phenylurethane and of hydrocyanic acid on the carbon dioxide assimilation and on the respiration of algæ was also studied. S. S. Z.

Adsorption and Modification of Food Materials by Plants. E. Reinau (*Zeitsch. Elektrochem.*, 1920, **26**, 329—342). Corresponding with the theory of the assimilation of carbon dioxide by plants, a similar hypothesis is proposed for the other elementary food materials, and conclusions are drawn therefrom for the complete metabolism of plants; the idea of physiological concentration receives an explanation thereby. The different stages passed through by the elementary food materials are somewhat as follows: acceptor compound, assimilation substances of varying complexity, acceptor substance, acceptogen, structure material and reserve matter, degradation products. The natural periodic sequence in the formation of these different substances necessitates a continuously varying provision of the corresponding elementary food materials to the plant. To secure the highest cultural result, therefore, the metabolism for each specific element must be separately considered. The various individual metabolisms are, however, inseparably connected since the elementary food materials, singly or in conjunction, may in the form of acceptor substance chemically or physically attract another elementary food material. The hydrostatic osmotic action of carbon metabolism towards water in plants is considered, and from this point of view the connexion between the phenomena of the nutrient salt economics of plants and the height of their growth is explained. In the light of the author's theory, a simple explanation of the relationship between the increase of a vegetation factor and the mass production of plants is given. Certain peculiar phenomena observed in the carbon-dioxide manuring of plants are brought into the general scheme of metabolism.

Certain analogies to the principles of material metabolism in plants are shown when changes of energy are considered.

All the conceptions thus developed depend on the lytic properties of water and the associations and dissociations which occur within the individual cell surrounded by walls of varying permeability.

It is further shown that the elementary food materials consist of substances of low atomic or molecular weight, that the continuously increasing condensation and formation of insoluble products direct the stream of nutrient material in a definite direction, and that this action is supplemented by the behaviour of the condensation products at the differently permeable cell walls whereby the backward flow of the elementary substances is hindered. H. W.

Formaldehyde as an Intermediate Stage between the Real Assimilation and the Formation of Carbohydrates in Plants. MARTIN JACOBY (*Biochem. Zeitsch.*, 1919, **101**, 1—6).—Leaves of *Tropaeolum majus* were exposed to formaldehyde in the dark, and it was found that an increase in the dry matter took place in these leaves as compared with control leaves when certain conditions were observed. The author considers that the formaldehyde was not fixed, but actually transformed into tissue of the plant. S. S. Z.

Selective Absorption of Ions from Equilibrated Solutions. E. PANTANELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1920, **26**, 136—151).—Experiments have been made on the absorption of the different ions in salt solutions by marine algæ and by terrestrial plants. T. H. P.

Distribution of Lycorine in the N.O. Amaryllidaceæ. II. K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], **2**, 331—334. Compare this vol., i, 467).—The crystallised alkaloid has been isolated from the bulbs and roots of *Amaryllis Belladonna*, L., *Clivia miniata*, Benth., *Cooperia Drummondii*, Herb., *Cyrtanthus pallidus*, Sims, and *Sprekelia formosissima*, Herb. (yield, 0·1—0·01% and less). It is doubtless identical with "belamarine" from the first-named species and with "amarylline" from the last-named, both isolated by Fragner (A., 1891, 1122), and also with the veratrine-like alkaloid obtained by Molle from the second species (*Jahresb. Pharm.*, 1903, 27). G. B.

Constituents of Digitalis. WILLIAM J. MCGILL (*J. Amer. Chem. Soc.*, 1920, **42**, 1893—1900).—By careful manipulation and uniform methods of procedure, using various solvents, it is possible to obtain crude fractions from digitalis which will have a reasonably constant chemical composition. The cold water extract of the leaves contains either none or a very minute quantity of digitoxin, its activity being entirely due to two fractions, soluble and insoluble in chloroform respectively (compare Kraft, A., 1912, i, 373). The digitsaponin of digitalis leaves is found to be totally inactive and non-hæmolytic when purified. The chloroform-soluble fraction obtained by Hatcher (compare *J. Amer. Pharm. Assoc.*, 1919, **8**, 913) from the hot water extract of the leaves is a mixture of gitalin and digitoxin. W. G.

The Appearance and the Emulsifying Action of Various Substances in the Cells of the Leaves of Fontinalis antipyretica. KARL BORESCH (*Biochem. Zeitsch.*, 1919, **101**, 110—158).—The fatty nature of the thread-like convolutions present in the cells of the leaves of *Fontalis antipyretica* has been established by means of microchemical methods. Alcohols, phenols, alkaloids and their salts, ammonia and its salts and its derivatives, produce the disintegration of these convolutions into small drops (emulsification). The emulsifying action of substances belonging to the groups mentioned has been studied in detail. S. S. Z.

"Taifushi" Oil. S. KEIMATSU (*J. Pharm. Soc. Japan*, 1920, 283—296).—"Taifushi" oil, m. p. 22—23°, D^{15} 0·952, $[\alpha]_D$ +51·2°, acid number 12·06, saponification number 20·30, iodine number 85·05, is the oleum gynocardiæ (oleum chaulmoogræ) of the Japanese pharmacopœia, but, in the author's opinion, is obtained from neither *Gynocardia edorata*, R. Br., nor *Taraktogenos kurzii*, King, but from the seeds of *Hydnocarpus anthelmintica*, Pierre. It contains palmitin, but its chief constituents are glyceryl chaulmoograte and hydnocarpate. A dihydroxyhydnocarpic acid, $C_{15}H_{27}(OH)_2 \cdot CO_2H$, m. p. 83°, is obtained by oxidising hyduocarpic acid at a low temperature. CHEMICAL ABSTRACTS.

Phytin. XVI. Occurrence of Inositolhexaphosphoric Acid in the Seed of the Silver Maple (Acer Saccharinum). R. J. ANDERSON [with W. L. KULP] (*J. Biol. Chem.*, 1920, **43**, 469—475).—From the freshly powdered maple seed, a crystalline barium salt corresponding with tribarium inositolhexaphosphate was isolated. The freshly powdered seed does not, apparently, contain any active phytase. The examination of a sample of seed which had been stored for some time showed that some hydrolysis of the organic phosphorus compounds had occurred, for the salt isolated was apparently a barium salt of inositolpentaphosphoric acid. J. C. D.

The Biochemical Method of Detection of Glucosides Hydrolysable by Emulsin. ÉM. BOURQUELOT (*Compt. rend.*, 1920, **171**, 423—425. Compare Delauney, succeeding abstract).—A brief review of the work accomplished by this method. W. G.

Extraction of Glucosides from Two Indigenous Orchids; Identification of these Glucosides with Loroglossin. P. DELAUNEY (*Compt. rend.*, 1920, **171**, 435—437).—The author has isolated from *Orchis Simia*, Lam., and *Ophrys aranifera*, Huds., a crystalline glucoside identical in each case with the loroglossin obtained from *Loroglossum hircinum*, Ric., by Bourquelot and Bridel (A., 1919, i, 243). W. G.

The Action of Pectase. HANS VON EULER and OLOF SVANBERG (*Biochem. Zeitsch.*, 1919, **100**, 271—278).—The coagulation of the juice of *Ribes nigrum* is not due to any change in the hydrogen ion concentration, but is brought about by the action of an enzyme. When the juice is heated at 95° or 75° for five minutes, no coagulation takes place after three days. The optimum H-ion concentration for the activity of the enzyme is $p_H = 4·3$. The pectase of *R. rubrum* coagulates the pectin of *R. nigrum*. S. S. Z.

The Formation of Melanin in Autolysed Potato Juice. HUGO HAEHN (*Biochem. Zeitsch.*, 1919, **100**, 114—129).—The dark coloration of potato juice is due to the formation of melanin by tyrosinase from the tyrosine of the juice. The "melanin value" is the number of c.c. of 0·002*N*-potassium permanganate necessary to decolorise 1 c.c. of boiled and filtered juice. During storage of potato juice at 37°, the proteins in it are autolysed and more tyrosine is set free, which is responsible for a higher "melanin

value." The difference in the "melanin value" before and aft autolysis—"the autolytic value"—varies with the different vari ties of potatoes. Six months' storage of the potato tuber produc an increase in the amino-acids, but a decrease in the tyrosinas The formation of melanin is increased in weakly alkaline solutic when the juice is stored in a warm place. S. S. Z.

Investigation of Plantago coronopus, L. EM. EMMANU and M. PAPAVASILION (*Arch. Pharm.*, 1920, **258**, 142—147).- The plant is indigenous to Greece and the surrounding countrie preparations of it are used as powerful diuretics.

The seeds yield 44·2% of mucus and 4·6% of a gum which soluble in water, shows the reactions of the pentoses, and converted by nitric acid into mucic acid.

The whole plant, excluding the seeds, was exhaustively extracte with alcohol (95%); the concentrated extract deposited sma quantities of chlorophyll and sodium chloride. The filtrate wa diluted with water containing sulphurous acid, and the precipitat formed separated by ether into insoluble *plantagenic aci* $C_9H_{12}O_2$, m. p. 210° (the *silver* salt was analysed), and solubl resin, acid number 73·39, saponification number 158·7, from whic sodium hydroxide solution extracted *coronopic acid*, $C_{54}H_{86}O$ amorphous, white mass, m. p. 281—282°, whilst from the portio left after this treatment a pale yellow, mobile essential oi n^{40} 1·6893, was obtained in very small amount by distillation wit steam, the remainder consisting of a *resin*, m. p. 128—130°, whic evolved benzoic acid when heated on platinum foil. The presenc of bitter principles or glucosides could not be detected, but emulsi and invertin were found by Bourdier's method.

The plant yields 7% of ash containing aluminium, magnesiun sodium, potassium, silica, chlorine, phosphoric and sulphuric acids the presence of lithium could not be detected spectroscopically The diuretic action of the plant, which has frequently bee attributed to the latter element, is probably due to its high conten in mucus. H. W.

The Ragweed Pollen Proteins. FREDERICK W. HEYL an HARRIS H. HOPKINS (*J. Amer. Chem. Soc.*, 1920, **42**, 1738—1743 Compare Heyl, A., 1919, i, 373).—The proteoses, the albumin, an the glutelin from ragweed pollen have been hydrolysed with 20% hydrochloric acid, and the various amino-acids, etc., estimated i the product by the Van Slyke process. Histidine is entirely absen from the proteoses and albumin. W. G.

Some Constituents of Viburnum prunifolium. FREDERIC W. HEYL and CHARLES BARKENBUS (*J. Amer. Chem. Soc.*, 1920 **42**, 1744—1755).—The dried root bark of *Viburnum prunifolium* was examined by the usual methods. Amongst the various pro ducts were acetic and valeric acids in the free state, as comple esters soluble in water and as resinous esters insoluble in water The resin insoluble in water contained a new *phytosterol*, m. p 186—187°, $[\alpha]_D$ +115° (in chloroform), giving an *acetate*, m. p 223—224°. The fat from this resin contained formic, acetic hexoic, octoic, myristic, palmitic, oleic, and linolic acids, but no

valeric acid. A trace of an amorphous alkaloid was found in the *alcoholic extract*. W. G.

Certain Physiological Actions of Osmium Tetroxide. RUD. SEELIGER (*Ber. Deut. bot. Ges.*, 1920, **38**, 176—184).—The wheat corn withstands for some hours, without being killed, relatively high concentrations of osmium tetroxide, although in lower concentrations this oxide retards *germination*, *delays growth*, and results in diminution of the magnitude of the organs of the young plant. The *parenchymatous* cells of the red beet are highly sensitive to the action of osmium tetroxide. T. H. P.

Ripening of Cereals. HEINRICH LÜERS (*Biochem. Zeitsch.* 1920, **104**, 30—81).—A new method is described of estimating acidity in organic extracts, the acid being titrated against both neutral-red and phenolphthalein in one and the same test liquid; this method gives reproducible results. An improvement is introduced into *Sörensen's formol-titration method*, the *end-point* being determined, not by means of azolitmin paper, but by titration in *presence* of neutral-red.

These two methods have been applied to follow the alterations in acidity, formol-titratable nitrogen, and enzymic relations of barley, wheat, oats, and rye during the last stages of ripening and subsequent storage for two months. The first two magnitudes diminish during the ripening, and, to a less extent, during storage, the acid passing into organic combination and the formol-titratable substances undergoing condensation to more highly complex compouuds. In most cases the enzymic properties become more marked as ripening proceeds, but in some instances a diminution, followed by an increase, occurs; the enzymic changes taking place in the ripening and resting corn are considered from different chemical, physical, and colloid-chemical points of view. T. H. P.

Effect of various Soluble Salts and Lime on Evaporation, Capillary Rise, and Distribution of Water in some Agricultural Soils. M. I. WOLKOFF (*Soil Sci.*, 1920, **9**, 409—436).—The salts used were ammonium, potassium, and magnesium sulphates, sodium chloride, calcium nitrate, potassium phosphate, and calcium oxide, these being applied at the rate of approximately 2510 kilos. per hectare to different types of soil. The results obtained varied considerably with the particular salt used and the soil to which it was applied. In general, soluble salts materially decrease the evaporation of soil moisture, there being apparently a direct relationship between the efficiency of the salts in this respect and the osmotic concentration of the soil solution in the surface 2·5 cm. of soil. The greater this osmotic concentration, the greater is the depression of the evaporation. Of the salts studied, sodium chloride and calcium nitrate were most effective and potassium sulphate and phosphate least effective in checking the evaporation. In this respect calcium oxide was least effective in sea sand and sandy loam and most effective in clay loam.

In two of the soils sodium chloride decreased the capillary rise, whilst calcium oxide in drab clay and potassium phosphate in a silt

loam tended to increase the rise, ammonium sulphate showing no pronounced effect.

In soils treated with sodium chloride, potassium phosphate or calcium oxide there was a pronounced tendency for an increase in the water content of the top 20 cm., and soil treated with potassium phosphate or calcium oxide contained more water even in the top inch than the untreated soil, although evaporation was decreased from the treated soil. W. G.

Distribution of Titanium in Soils and Plants. GEILMANN (*J. Landw.*, 1920, **68**, 107—124).—The estimation of titanium dioxide in soils may be carried out by a modification of Hillebrand's method ("Analysis of Silicate and Carbonate Rocks," see this vol., ii, 449). Titanium dioxide is widespread in soils in proportions varying from traces to 1%, the content generally lying between 0·3% and 0·6%. Of a number of plants examined, nearly all contain titanium, which occurs in largest proportion in the green parts of the plants. Plant ashes contain from traces to 0·27% of TiO_2. T. H. P.

Acid Clay and Acid Soil. KIUHEI KOBAYASHI (*J. Chem. Ind. Japan*, 1920, **23**, 549—555).—Reviewing theories on the acidity of soil, the author attributes the acidity to the adsorptive properties of Japanese acid clay or like substances mixed with it. (Compare this vol., i, 704). K. K.

The Importance of Liming Soils containing Humus. SVEN ODÉN (*Internat. Mitt. Bodenkunde*, **9**, 375—390; from *Chem. Zentr.*, 1920, iii, 396).—The favourable influence of lime on soils containing humus depends primarily on the formation of utilisable calcium humates. In this manner, toxic acids are neutralised, and formation of acid is hindered by the calcium humate. In addition, the calcium salts displace adsorbed nutrient matter, thus rendering it available for the plant. A marked effect on irrigation is not observed, but the oxidative capacity of the humic salts is a powerful factor. H. W.

Acidity of Mineral Acid Soils. S. OSUGI and T. UETSUKI (*Ber. Ohara Inst. landw. Forsch.*, 1916, **1**, 27—52; from *Chem. Zentr.*, 1920, iii, 395—396).—When the bases of the soil are rapidly diminished by marked weathering, colloidal substances are formed which adsorb the bases; free acids are obtained when such soils are treated with solutions of salts. Since the soil contains alumina and other compounds, which are readily decomposed by hydrochloric acid, but not by acetic acid, the filtrates from soils which have been treated with the former are rich in aluminium, whilst those obtained when potassium acetate is used contain but little of this metal. The differing intensities of the acidities of the filtrates thus obtained depend, in the first place, on the acid which has been liberated by the adsorption process in the soil. An acid soil must therefore be regarded as one which is incompletely saturated with bases. H. W.

Organic Chemistry.

Behaviour of Methane at High Temperatures Alone and in Contact with the other Constituents in Firedamp Explosions. H. Winter (*Brennstoff-Chem.*, 1920, **1**, 17—22).—In mixtures of pure methane and air containing from 5·0 to 9·2% of methane, the combustion occurs according to the equation $CH_4 + 2O_2 = CO_2 + 2H_2O$. In mixtures containing 9·2 to 14% of methane, the combustion of the methane is incomplete. In addition to carbon dioxide, water, and hydrogen, the residues contain carbon monoxide when the ratio of oxygen to methane is somewhat greater than, equal to, or less than, $O_2 : CH_4 = 2·0$. When the concentration of oxygen becomes smaller, hydrogen appears in addition to carbon dioxide and monoxide, nitrogen and water. The explosion under these conditions is also accompanied by deposition of carbon within a small area. J. R. P.

The Dehydrogenation of Alcohols by Catalytic Oxidation under Reduced Pressure. Charles Moureu and Georges Mignonac (*Compt. rend.*, 1920, **171**, 652).—The method previously described (this vol., i, 283) is modified so that the alcohol vapour and oxygen are passed, at a reduced pressure of 20—40 mm., over the catalyst, finely divided silver, at 230—300°. Under these conditions, satisfactory results are obtained with the higher alcohols. W. G.

The Reaction between Alcohols and Aqueous Solutions of Hydrochloric and Hydrobromic Acids. II. James F. Norris and Robert S. Mulliken (*J. Amer. Chem. Soc.*, 1920, **42**, 2093—2098).—In continuation of previous work (A., 1916, i, 461), it is shown that aqueous hydrobromic acid reacts with certain di- and tri-hydroxy-alcohols and certain cyclic alcohols. Hydrochloric acid replaced the hydroxyl group in certain of the alcohols containing negative substituents, but its failure to act in other cases indicated that influences other than those of negative groups serve to activate the hydroxyl group. W. G.

Chloromethyl Carbonates: Systematic Chlorination of Methyl Carbonate. André Kling, D. Florentin, and E. Jacob (*Ann. Chim.*, 1920, [ix], **14**, 189—214).—A more detailed account of work already published (this vol., i, 213). W. G.

New Syntheses of α-Monoglycerides. Emil Fischer, Max Bergmann, and Heinrich Bärwind (*Ber.*, 1920, **53**, [*B*], 1589—1605).—The general methods for the preparation of mono- and di-glycerides depend either on the action of glyceryl chlorohydrins on the salts of fatty acids or on esterification of the fatty acid with the chlorohydrin, and subsequent exchange of the halogen atoms for the hydroxyl group. Neither process is suitable

for synthetic operations, since the former method is complicated by side reactions, and no guarantee is afforded of the simple replacement of the halogen atom by the fatty radicle (compare Fischer, Bergmann, and Lipschitz, A., 1918, i, 172), whilst in the latter the halogen atom can, in general, be only replaced under conditions which readily occasion further change. As initial material in a new series of syntheses, the authors have therefore adopted "acetone glycerol," which has been shown by Irvine, Macdonald, and Soutar (T., 1915, **107**, 337) to be *iso*propylideneglycerol, $CMe_2<\begin{matrix}O\cdot CH_2\\ O\cdot CH\cdot CH_2\cdot OH\end{matrix}$; this substance reacts readily with acid chlorides in the presence of quinoline, yielding products, from which the acetone residue is readily removed by mild treatment, thus giving undoubted α-monoglycerides.

Benzoylisopropylideneglycerol, $CMe_2<\begin{matrix}O\cdot CH_2\\ O\cdot CH\cdot CH_2\cdot OBz\end{matrix}$, large, monoclinic crystals, $a:b:c=1.0221:1:0.4661$, $\beta=108°56'$, m. p. 34·5°, b. p. 164—165°/9—10 mm., is readily obtained by the action of benzoyl chloride on an ice-cold mixture of *iso*propylideneglycerol and quinoline, and is transformed by $N/2$-hydrochloric acid at 55—60° into α-monobenzoylglycerol, m. p. 36° (compare Krafft, A., 1904, i, 136), which is partly decomposed on distillation, even in a high vacuum, into glycerol and dibenzoylglycerol; it re-forms the *iso*propylidene compound in good yield when treated with dry acetone containing 1% of hydrogen chloride, and with phenylcarbimide gives the corresponding diphenylurethane, small needles arranged in clusters, m. p. 135—136° (corr.). p-*Nitrobenzoylisopropylideneglycerol*, leaflets, m. p. 56°, and α-p-*nitrobenzoylglycerol*, pale yellow prisms, m. p. 107°, are similarly prepared; the latter is converted by benzoyl chloride in the presence of chloroform and pyridine into *βγ-dibenzoyl-α-p-nitrobenzoylglycerol*, $NO_2\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CH(OBz)\cdot CH_2\cdot OBz$, colourless, four-sided needles, m. p. 114° (corr.).

Stearyl chloride, b. p. 164—166°/0·5—1 mm., transforms *iso*propylideneglycerol into *stearylisopropylideneglycerol*, long, colourless needles, m. p. 40—41° after slight softening at 37°, which is converted by aqueous hydrochloric acid in the presence of ether into α-monostearin, which generally has m. p. 81—82°; a second modification, m. p. 75—76°, is obtained when the first form is melted and allowed to solidify or rapidly crystallised from ether. *Laurylisopropylideneglycerol*, pale yellow, mobile oil, has b. p. 151—152°/0·2—0·3 mm., m. p. +8—9°, D_4^{13} 0·9537, n_D^{13} 1·4454, whilst α-monolaurin forms small, unctuous leaflets, m. p. 62—63° (Krafft, *loc. cit.*, gives m. p. 59°, Grün and von Skopnik, A., 1909, i, 874, 52°, and Thieme, A., 1912, i, 333, 58·9°). α-Monolaurin is converted by phenylcarbimide into the *diphenylurethane*, small leaflets, which generally have m. p. 87—89°, but for which, on one occasion, the m. p. 92—94°, returning to the normal value after some weeks, was observed, and by stearyl chloride into α-lauryl-βγ-distearylglycerol, m. p. 49—50°, apparently identical

with the product described by Grün and Theimer (A., 1907, i, 464). *Palmityl*iso*propylideneglycerol* crystallises in thin, irregular leaflets, m. p. 34—35°, whilst α-monopalmitin resembles α-monostearin in forming two modifications, m. p. 78—79° and 72—73°, respectively, which are prepared in the same manner as the stearyl compounds. It is transformed by lauryl chloride in the presence of chloroform and pyridine into *βγ-dilauryl-α-palmitylglycerol*, small, slender needles, m. p. 47—48°, after slight softening at 45°, the melting point of the solidified material being the same as that of the original substance. H. W.

Acetone Glycerol [*iso*Propylideneglycerol] and its Applicability to the Preparation of Pure α-Glycerides; A Compound of Phosphoric Acid and Glycol. EMIL FISCHER and ERNST PFÄHLER (*Ber.*, 1920, **53**, [*B*], 1606—1621).—The present communication is devoted to a general survey of the possibility of using *iso*propylideneglycerol in the syntheses of pure α-monoglycerides (compare preceding abstract). Further confirmation of the constitution assigned to the substance by Irvine, Macdonald, and Soutar (T., 1915, **107**, 337) is found in that trimethylene glycol does not condense with acetone under conditions which readily yield products with ethylene and propylene glycols and with glycerol α-chloro- and α-iodo-hydrin. The introduction of the dihydroxypropyl complex into other substances appears to be most readily effected by means of *iso*propylideneglycerol-α-iodohydrin; the chlorine atom of the chlorohydrin is too firmly retained for this purpose.

*iso*Propylideneglycerol is prepared in 77% yield by the treatment of anhydrous glycerol with dry acetone containing 1% of hydrogen chloride in the presence of anhydrous sodium sulphate at the ordinary temperature; the bulk of the acid is removed by agitation with lead carbonate, and the filtrate is fractionated in the presence of a little silver oxide; the substance has b. p. 82·5°/11 mm., D_4^{20} 1·0678, D_4^{14} 1·0721, n_D^{20} 1·43509.

iso*Propylideneglycerol-α-chlorohydrin*, b. p. 157°/767 mm., D_4^{15} 1·109, D_4^{20} 1·1079, n_D^{15} 1·43750, is obtained from glycerol-α-chlorohydrin, b. p. 113°/10 mm. (which is conveniently prepared by the protracted boiling of *epi*chlorohydrin with water); it is unaffected by aqueous acetone at 100°, and only slowly attacked by an excess of aqueous potassium hydroxide at 125° or by methyl-alcoholic ammonia at 100°. Protracted heating with sodium iodide and alcohol at 100° transforms it into glycerol-α-iodohydrin, m. p. 49—50°.

iso*Propylideneglycerol-α-iodohydrin*, $CMe_2<\begin{matrix}O\cdot CH_2\\ O\cdot CH\cdot CH_2I\end{matrix}$, b. p. 79°/10 mm., $D_4^{15\cdot5}$ 1·652, $D_4^{18\cdot5}$ 1·648, $n_D^{15\cdot5}$ 1·50589, $n_D^{18\cdot5}$ 1·50460, condenses with ethyl sodiomalonate in ethyl-alcoholic solution *to ethyl βγ-*iso*propylidenedioxypropylmalonate*,

colourless oil, b. p. 155—156°/10 mm. (the *lead* salt, broad needle or leaflets, $+H_2O$, and the *calcium* salt, needles, $+2\cdot5H_2O$, of th corresponding acid, are described).

iso*Propylideneglycerol acetate*, mobile oil, b. p. 84°/9 mm., 87° 12 mm., D_4^{15} 1·0771, n_D^{15} 1·42911, is obtained in 83% yield by th action of acetic anhydride and pyridine on *iso*propylideneglycerol and is converted by N/4-sulphuric acid at 45° into α-monoacetin b. p. 103°/0·4 mm.; even at the lowest possible pressure, som slight decomposition occurs during distillation, and this increase rapidly in proportion as the pressure is raised. For syntheti purposes, it is therefore preferable to use the undistilled com pound. (This observation makes it very probable that all th mono- and di-glycerides previously described, and purified by dis tillation under a pressure of 10 mm. and more, are not homo geneous.) α-Monoacetin reacts with *p*-nitrobenzoyl chloride i the presence of chloroform and pyridine to yield *glyceryl βγ-di-p nitrobenzoate α-acetate*, microscopic, three-sided platelets, m. p 129—130° (corr.); attempts to eliminate the acetyl group b methyl-alcoholic ammonia, and thus to obtain αβ-di-*p*-nitrobenzoyl glycerol, did not lead to the desired results, since total alcoholysi occurred.

*iso*Propylideneglycerol is converted by phosphoryl chloride an quinoline at $-20°$ into *βγ-isopropylidenedioxypropyl phosphate*

$$CMe_2<\begin{matrix}O\cdot CH_2\\ O\cdot CH\cdot CH_2\cdot O\cdot PO(OH)_2\end{matrix}$$

which is isolated in the form o its *barium* salt, shining platelets ($+3H_2O$); 3·64 parts of th anhydrous *salt* dissolve in 100 parts of water at 25°. The corre sponding *silver*, *lead*, and *mercury* salts are described. Th barium salt is transformed by sulphuric acid into α-glyceryl phos phate, which is isolated as the readily soluble amorphous o sparingly soluble crystalline barium salt (the *silver* salt, colourles needles, is described). *Diisopropylideneglycerol monophosphate* i contained in the mother liquors obtained in the experiment just described, and is isolated as the readily soluble *barium* salt, $C_{24}H_{44}O_{16}P_2Ba$ (the corresponding *lead*, *silver*, and *mercury* salts are described); acetone is removed by treatment with dilut sulphuric acid, thereby yielding *diglycerol monophosphate*, $[OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O]_2\cdot PO\cdot OH$, which is obtained as th amorphous barium salt; the corresponding *silver*, *lead*, *mercury*, *copper*, and *zinc* salts are freely soluble in water.

Ethylene glycol is transformed by phosphoryl chloride and pyridine at $-20°$ into *β-chloroethyl phosphate*,

$$CH_2Cl\cdot CH_2\cdot O\cdot PO(OH)_2,$$

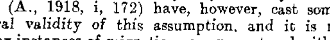
which is isolated as the *barium* salt, colourless needles ($+3H_2O$); the corresponding *silver* salt, slender needles, and *lead* salt, colourless, amorphous precipitate, are described. H. W.

Wandering of Acyl Groups in Glycerides. EMIL FISCHER (*Ber.*, 1920, **53**, [*B*], 1621—1633).—In previous syntheses of glycerides it has generally been assumed that the acyl groups

retain their respective positions in the molecule when other substituents, such as halogen atoms, are removed. The observations of Fischer, Bergmann, and Lipschitz on the migration of acyl groups during the partial hydrolysis of acylated phenolcarboxylic acids (A., 1918, i, 172) have, however, cast some doubt on the general validity of this assumption, and it is now shown that similar instances of migration are encountered with glycerides. The problem is investigated in the following manner. On the one hand, an *α*-monoacylglycerol, $OA \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, is converted by an acid chloride, BCl, in the presence of pyridine or quinoline into the mixed triglyceride, $OA \cdot CH_2 \cdot CH(OB) \cdot CH_2 \cdot OB$; on the other hand, glycerol *α*-iodohydrin is transformed by BCl into the diacyl iodohydrin, $CH_2I \cdot CH(OB) \cdot CH_2 \cdot OB$, which would be expected to be converted into the diacyl derivative,

$$OH \cdot CH_2 \cdot CH(OB) \cdot CH_2 \cdot OB,$$

which, by treatment with ACl, should pass into the mixed triglyceride, $OA \cdot CH_2 \cdot CH(OB) \cdot CH_2 \cdot OB$, identical with that obtained by the first process. Actually, however, it is found that an isomeride of higher melting point and smaller solubility is produced, so that a displacement of an acyl group must have occurred during one of the changes. It appears probable that the migration of the acyl group from the *β*- to the *α*-position occurs at the stage of the elimination of iodine, and although at present it is impossible to give an exact account of the mechanism of the change, it is suggested that an intermediate compound of the type,



(in the case of the di-*p*-nitrobenzoyl derivative) is produced. *αα'*-Diglycerides are obtained with such readiness from *αβ*-diacyl-*γ*-iodohydrins that this constitutes their readiest method of preparation. A somewhat similar series of actions has been effected by Grün and Schreyer (A., 1913, i, 159) with the corresponding chlorohydrins, but it is thus rendered highly probable that their "*αβ*-diglycerides" are really *αγ*-compounds.

γ-Iodohydrin αβ-di-p-nitrobenzoate,

$$CH_2I \cdot CH(O \cdot CO \cdot C_6H_4 \cdot NO_2) \cdot CH_2 \cdot O \cdot CO \cdot C_6H_4 \cdot NO_2,$$

pointed needles, m. p. 102—103°, is obtained by the interaction of *p*-nitrobenzoyl chloride and *α*-iodohydrin (alival) in the presence of chloroform and pyridine, and is converted by silver nitrite in boiling aqueous propyl-alcoholic solution or of silver acetate in the presence of warm glacial acetic acid into *glycerol αγ-di-p-nitrobenzoate*, $OH \cdot CH(CH_2 \cdot O \cdot CO \cdot C_6H_4 \cdot NO_2)_2$, thin, colourless, four-sided, rhombic leaflets, m. p. 136—137° (corr.). The latter is converted by acetic anhydride in the presence of dry pyridine at the ordinary temperature into the corresponding *β-acetyl* derivative, long, slender needles, m. p. 161° (corr.).

γ-Iodohydrin αβ-distearate, small needles, m. p. 52—53°, is similarly converted successively into *αγ-distearin*, colourless, broad needles or platelets, m. p. 78·5—79° (corr.), and *glyceryl β-acetate αγ-distearate*, silky needles, m. p. 64°. *Glyceryl α-acetate βγ-*

distearate (from pure α-monoacetin and stearyl chloride in the presence of chloroform and quinoline) crystallises in needles, m. p. 59°.

*Glyceryl α-benzoate βγ-di-*p*-nitrobenzoate* crystallises in long, colourless needles, m. p. 122—123° (corr.), whilst the isomeric *glyceryl β-benzoate αγ-di-*p*-nitrobenzoate,* long, four-sided rods, has m. p. 152—152·5° (corr.). Similarly, *glyceryl α-*p*-nitrobenzoate βγ-distearate* forms slender, silky needles, m. p. 74·5°, and *glyceryl β-*p*-nitrobenzoate αγ-distearate* crystallises in slender needles, m. p. 61°. *γ-Iodohydrin αβ-dibenzoate,* long, colourless needles, has m. p. 56—57°. *Di-iodohydrin* p*-nitrobenzoate,* from *p*-nitrobenzoyl chloride and the di-iodohydrin (Jothion) in the presence of chloroform and pyridine, forms microscopic, four-sided prisms, m. p. 82—83° (corr.). H. W.

Interaction of Ethylene and Selenium Monochloride. Harold William Bausor, Charles Stanley Gibson, and William Jackson Pope (T., 1920, **117**, 1453—1456).

The Influence of Electrolytic Dissociation on the Distillation in Steam of the Volatile Fatty Acids. Joseph Reilly and Wilfred J. Hickinbottom (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 120—130).—When dilute solutions of volatile fatty acids are distilled, they show deviations in their distillation constants. These results cannot be explained on the basis of the possible occurrence of molecular complexes in the solution or of hydration of the solute. The deviations are probably due to electrolytic dissociation, since the deviation increases with the dilution, and is most marked with acids possessing a comparatively large dissociation constant. The authors have deduced a mathematical expression to represent this dissociation during distillation, and thus to correct the distillation constant. Applying this correction, it is found that the distillation constant is practically independent of the dilution.

The addition of certain salts and acids increases the distillation constant of acetic acid, but the amount of increase is dependent on the nature of the salt added. The addition of a solution of copper sulphate containing 1 gram-mol. per litre to a dilute acetic acid solution causes a diminution in the distillation constant.

W. G.

Preparation of Ethylidene Diacetate. Société Chimique des Usines du Rhône Anct. Gilliard, P. Monnet et Cartier (D.R.-P. 322746; from *Chem. Zentr.*, 1920, iv, 437).—Acetylene is treated with acetic acid and mercury salts in the presence of catalysing agents, the use of mercuric acetate and sulphuric esters being particularly cited. Acetylene is very rapidly absorbed in the presence of methylene sulphate at 40—65°, or of methyl sulphate at 70—80°, and the harmful effect of free mineral acids is avoided. Ethylidene diacetate, purified by fractional distillation in a

acuum after addition of sodium acetate, is obtained in almost ıeoretical yield. H. W.

Anhydrides of the Higher Aliphatic Fatty Acids. III.). HOLDE and H. SMELKUS (*Ber.*, 1920, **53**, [*B*], 1889—1897).—'he preparation and purification of the anhydrides of the higher ıtty acids have been investigated, more particularly in connexion ith their possible use as articles of food in place of the glyceride ıts. The material employed was the mixture of fatty acids from nseed oil and commercial olein, which was purified by distillation nder diminished pressure. Albitzky's method of dehydration by ıeans of acetic anhydride at 150—160° was adopted, and it was ound that the proportion of anhydride recommended (5·5 times hat theoretically necessary) is undoubtedly in excess of that ctually required; the crude anhydrides cannot be freed from acetic cid and excess of anhydride by treatment with steam, since they re thereby almost entirely converted into fatty acids, and the ields of anhydrides cannot be estimated by titration of the proucts with $N/10$- or $N/20$-alcoholic alkali, since the anhydride is lowly converted into a mixture of the ethyl ester and sodium salt f the fatty acid. Attempts to separate the anhydrides from the atty acids by means of alcohol were not successful, since, although he fatty acids from linseed oil, for example, are completely soluble n 72% alcohol (by volume), whilst the anhydrides are almost ısoluble, the solubility of the latter is considerably affected by the resence of the former, possibly also by the formation of ethyl sters. With stronger alcohol, the solubility of the anhydrides in he presence of the fatty acids is uniformly greatly increased.)istillation under diminished pressure is unsuitable for the separ-ation of oleic anhydride and oleic acid, since the former is decom-osed during the process; as this has also been shown to be the ase with palmitic acid, it appears to be true generally for the igher fatty acids and their anhydrides. The only satisfactory ıethod appears to consist in treating the mixtures with solid odium carbonate or with aqueous solutions of the latter.

H. W.

Anhydrides of the Higher Aliphatic Fatty Acids. IV.). HOLDE and IDA TACKE (*Ber.*, 1920, **53**, [*B*], 1898—1907. 'ompare preceding abstract).—*Further experiments on the pre-aration and properties of the mixtures of fatty anhydrides,* btained by the action of acetic anhydride on the fatty acids of inseed and rape-seed oil and on oleic acid, are described, particu-arly with a view to the possibility of their substitution for fats as oods. The proportion of acetic anhydride can be reduced to 3·5 imes that theoretically necessary without reducing the yield below 3·5% (possibly this proportion can be still further reduced and he dehydration performed under ordinary pressure). Excess of he reagents is removed by distillation under diminished pressure, nd further purification of the anhydrides is effected by treatment

with powdered sodium carbonate or aqueous sodium carbonate solution (5%). The purity of the products is conveniently examined by determination of the molecular weight in benzene solution. The mixtures of anhydrides have generally a somewhat higher melting point than the fatty acids from which they are derived, and, at the ordinary temperature, are semi-solid and sometimes partly crystalline. The viscosity and volatility is about the same as those of the corresponding glycerides, which they also closely resemble in refractive index. They are decomposed by $N/10$ or more dilute alcoholic alkali hydroxide solution into almost exactly equivalent amounts of alkali salt and ethyl ester of the fatty acids, but the so-called saponification number can be estimated accurately with $N/2$-alcoholic potassium hydroxide. Mixed anhydrides of the fatty acid and acetic acid are not present in the products.

H. W.

The Alkali Lactates as Substitutes for Glycerol [Per- and Perka-glycerin]. CARL NEUBERG and ELSA REINFURTH (*Ber.*, 1920, **53**, [*B*], 1783—1791).—Apart from its use in the production of explosives, glycerol is extensively applied technically to the production of plastic masses, as a lubricant, as a solvent for heating baths, for the preservation of anatomical preparations and surgical instruments, and for pharmaceutical purposes. Its many-sided applicability depends mainly on its viscosity, hygroscopicity, and neutral character. The shortage of natural sources of glycerol experienced by the Central Powers during the war has directed attention to possible substitutes, which have been found in aqueous solutions of the sodium and potassium salts of fermentation lactic acid (per- and perka-glycerin respectively). As generally prepared, both salts consist of colourless, viscous substances with a not unpleasant saline taste, which are stable at elevated temperatures, and pronouncedly hygroscopic. They only crystallise when in a very highly purified condition, and readily yield strongly supersaturated solutions, which are miscible in all proportions with water and alcohol. They are not poisonous, and do not irritate the membranes. They have this economic advantage over glycerol, that their preparation permits a much better utilisation of the initial material (sugar, etc.), since this can be so fermented as to yield 95% and more lactic acid, whilst, on the technical scale, it only gives one-fifth to one-fourth of its weight of glycerol; further, for many purposes, the glycerol substitutes can be used in more dilute solution than glycerol itself. An extended account is given of the application of the substitutes in the armies and navies of the Central Powers, and of their use for medical and cosmetic purposes, for details of which the original paper must be consulted; in general, however, it may be stated that they well fulfil all the non-explosive purposes to which glycerol is usually applied.

It has been observed during the industrial preparation of sodium and potassium lactates that these salts can be crystallised from highly concentrated aqueous solutions, but the solid preparations

do not give uniform results on analysis, since the fermentation acid is a mixture of racemic and optically active lactic acids.

Tables and graphs are given showing the densities of aqueous solutions of "per- and perka-glycerin" at 15°, the freezing point of solutions of "perglycerin" at differing concentrations, the comparative freezing points of solutions of "perglycerin" and glycerol of similar molecular concentrations, the boiling points of solutions of "perglycerin," the comparative hygroscopicity of solutions of "perglycerin" and glycerol at 25°, and the viscosity of "perglycerin." H. W.

The Methodical Degradation of Saturated Dibasic Acids of High Molecular Weight. MARCEL GODCHOT (*Compt. rend.*, 1920, **171**, 797—799).—The method used by Bouveault and by Barbier and Locquin (A., 1913, i, 700) for the conversion of saturated bibasic acids into corresponding acids containing two atoms less of carbon is found to be applicable to the higher acids in the series.

Thus, ethyl suberate yields with magnesium phenyl bromide *ααθθ-tetraphenyloctane-αθ-diol*, m. p. 112—113°, which, when dehydrated, gives *ααθθ-tetraphenylocta-Δ^{αθ}-diene*,

$$CPh_2{:}CH\cdot[CH_2]_4\cdot CH{:}CPh_2,$$

m. p. 92—93°, and this, on oxidation, gives adipic acid.

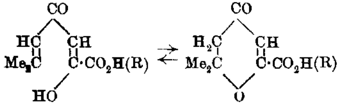
In a similar manner, ethyl azelate gives, in turn, *ααιι-tetraphenylnonane-αι-diol*, m. p. 136°, *ααιι-tetraphenylnona-Δ^{αι}-diene*, b. p. 310°/20 mm., D^{20} 1·047, and pimelic acid, whilst ethyl sebacate gives *αακκ-tetraphenyldecane-ακ-diol*, m. p. 131—132°, *αακκ-tetraphenyldeca-Δ^{ακ}-diene*, m. p. 107°, and suberic acid. W. G.

The Isomeric Forms of Mesityloxidoxalic Acid and its Esters. W. DIECKMANN (*Ber.*, 1920, **53**, [*B*], 1772—1782).—The α- and β-forms of mesityloxidoxalic acid and its esters have generally been regarded as typical cases of keto-enolic desmotropy (compare Claisen, A., 1896, i, 557; Dimroth, A., 1907, i, 663; Michael and Hibbert, A., 1907, i, 1010; 1908, i, 28; Michael and Murphy, A., 1908, i, 949; K. H. Meyer, A., 1911, i, 865). The α-compounds are, beyond doubt, enolic forms, but, on the other hand, the conception of the β-compounds as ketones is no longer tenable. The behaviour of oxalyl derivatives of the type

$$R\cdot CO\cdot CH_2\cdot CO\cdot CO_2R$$

is generally in accordance with Claisen's rule that the tendency towards enolisation and the enol content of the equilibrium mixture increase with increasing acidity of the acyl groups; with mesityloxidoxalic esters, however, the equilibrium mixture contains only a small percentage of the enolic form, and, further, the α-ester, when distilled, passes mainly into the neutral β-ester. It is likewise remarkable that, whereas the enolic forms of acetophenoneoxalic acid and propionylpyruvic acid can be crystallised unchanged from boiling water, α-mesityloxidoxalic acid passes

completely into the β-acid when treated in this manner. Simila anomalies are exhibited by α-mesityloxidoxalic acid with respe to its rate of transformation in alcoholic solution; with substanc of the type $R·CO·CH_2·CO·R'$, equilibrium is generally establishe at 25° in the absence of catalysts within a day, and the rate c transformation is very greatly catalysed by alkaline agents, and t a very much smaller extent by acids; with α-mesityloxidoxalic este the change proceeds so slowly at the atmospheric temperature tha equilibrium is only attained after several months, the velocity c transformation is catalytically influenced to an unusually smal degree by alkaline agents, but very markedly by acids, even a very small concentrations. It therefore appears that the α- an β-forms cannot be regarded as keto-enolic desmotropes, and thei isomerism is attri buted to the con version of th α-forms by rin closure into d hydro - γ - pyron derivatives, accorc ing to the annexe



scheme. This conception is in harmony with the observed equi ibrium relationships and rates of transformation, and generall interprets the chemical behaviour of the β-forms better than doe the ketonic formula. It thus explains Claisen's observation that th aniline salt of the β-acid, in contrast to that of the α-acid, does nc pass into the anil in hot alcoholic solution, and the fact tha whereas α-mesityloxidoxalic acid and its esters are readily con verted by phenylhydrazine into phenylpyrazole derivatives, th β-acid and its esters yield normal phenylhydrazones, which do no pass into pyrazoles, even after protracted warming with glacia acetic acid. The physical properties of the β-forms are shown t be in harmony with the dihydropyrone formula. It is remarkabl that Claisen, in his preliminary note on these compounds (*Ber* 1891, **24**, 115), considered that the β-varieties are dihydropyron derivatives, but that this conception is abandoned in the subse quent fuller account (*loc. cit.*) in favour of the ketonic structure.

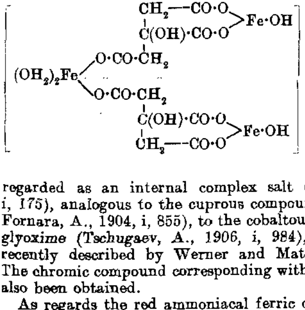
Methyl α-mesityloxidoxalate is converted by phenylhydrazine i glacial acetic acid solution into *methyl* 1-*phenyl*-5-Δ^{α}-iso *butenylpyrazole*-3-*carboxylate*, $Me_2C{:}CH·\underset{PhN——}{C}{:}CH·\underset{N}{C}·CO_2Me$, colourles crystals, m. p. 108°, which is hydrolysed by alkali to the corre sponding *acid*, colourless needles, m. p. 167° (which is also obtaine from the α-acid and phenylhydrazine in acetic or hydrochloric aci solution); the methyl ester of the β-compound gives the *phenyl hydrazone* of *methyl* 2:2-*dimethyl*-2:3-*dihydro*-γ-*pyrone*-6-*carb oxylate*, intensely yellow crystals, m. p. 163°. H. W.

Organic Salts of Iron. II. Ferric Citrates an Ammoniacal Ferric Citrates. E. Belloni (*Gazzetta*, 1920 **50**, ii, 159—212. Compare A., 1909, i, 283).—The author dis

cusses the literature, dealing, first, with complex organic cations and anions containing iron, and, secondly, with the chemistry of the ferric and ammoniacal ferric citrates. All the hypotheses which have been advanced to explain the structure of ammoniacal citrates of iron are based on the existence of normal ferric citrate, $C_6H_5O_7Fe$, which has been assumed from the results of old, insecure analyses. The chemical behaviour of ferric citrate renders it probable that the iron is present as a complex cation, and the concordant results of analyses of different preparations of the citrate lead to the formula $[Fe_3(C_6H_5O_7)_2(OH)_2]\frac{1}{3}C_6H_5O_7,8H_2O$. The citrate represents, indeed, a dicitratoferric citrate, in which there appears a new term of the series of univalent cations, $\left[\begin{matrix} X_6 \\ Fe_3(OH)_2 \end{matrix}\right]$, where X indicates a univalent acid radicle. The base,

$$[Fe_3(C_6H_5O_7)_2(OH)_2]OH,$$

of the citrate forms also a platinichloride, the existence of which confirms the fact that only one-seventh of the combined citric acid of the citrate is ionisable. The structure of the citratoferric ion must be analogous to that established in the case of ferric formate (*loc. cit.*), and confirmed by Weinland and Gussmann (A., 1909, i, 872; 1910, i, 296, 457, 537) and Herz (A., 1899, i, 416) for ferric and chromiferric acetates, and is shown in the annexed formula.



This complex ion differs from those of other organic iron salts in that the central iron atom is united to two citric radicles, which are held in the complex by both a principal and a secondary valency. Ferric citrate must hence be regarded as an internal complex salt (compare Ley, A., 1905, i, 175), analogous to the cuprous compound of glycine (Bruni and Fornara, A., 1904, i, 855), to the cobaltous compounds of dimethylglyoxime (Tschugaev, A., 1906, i, 984), and to the compounds recently described by Werner and Matissen (A., 1918, i, 379). The chromic compound corresponding with this ferric compound has also been obtained.

As regards the red ammoniacal ferric citrate, obtained by addition of ammonia to a solution of the dicitratotriferric citrate, it is found that four molecules of any alkali are absorbed by the dicitratotriferric cation without disturbance of the equilibrium permitting of the existence of this complex; further addition of an energetic alkali destroys the complex, but excess of ammonia does not affect the new complex. The composition of the ammoniacal product, the fact that $2H_2O$ is eliminated only at 120°, and its chemical properties, indicate that it is diaquodiferryl-

citratotetramminoferric citrate. With only 2 mols. of ammoni ferric citrate forms diaquocitratoferrylcitratodiammino-oldiferri citrate. With both these ammoniacal ferric citrates, only on seventh of the combined citric acid is ionisable, and the correspon ing platinichlorides have been obtained. The tetrammino-citrat (1 mol.), like other ferric salts, is able to dissolve excess of ferr hydroxide (up to 6·66 mols.); the solutions thus obtained may b concentrated without undergoing change, and then yield scal products, which increase in brittleness and opacity as the pe centage of dissolved hydroxide increases.

The interaction in the hot of 2 mols. of ferric hydroxide an 3 mols. of citric acid yields tricitratodiferric acid,

$$[Fe_2(C_6H_4O_7)_3]H_6,$$

and treatment of this with 3 mols. of ammonia gives the tr ammonium ferricitrate, $[Fe_2(C_6H_4O_7)_3](NH_4)_3H_3$, which is the gree ammoniacal ferric citrate used pharmaceutically. The mon ammonium and diammonium salts were also prepared.

Diaquodicitratodioltriferric citrate,

$$[Fe_3(C_6H_5O_7)_2(OH)_2(OH_2)_2]\tfrac{1}{3}C_6H_5O_7,6H_2O,$$

forms a reddish-yellow precipitate, and the *platinichloride*,

$$[Fe_3(C_6H_5O_7)_2(OH)_2]\tfrac{1}{2}PtCl_6,5H_2O,$$

a reddish-brown, crystalline powder.

Diaquodicitratodioltrichromic citrate,

$$[Cr_3(C_6H_5O_7)_2(OH)_2]\tfrac{1}{3}C_6H_5O_7,6H_2O,$$

forms blue scales with a violet reflexion, and the *platinichloride*, $[Cr_3(C_6H_5O_7)_2(OH)_2]\tfrac{1}{2}PtCl_6,5H_2O$, a violet, crystalline powder.

Diaquodiferrylcitratotetramminoferric citrate,

$$\{Fe[C_6H_4(FeO)O_7(NH_4)_2]_2(OH_2)_2\}\tfrac{1}{3}C_6H_5O_7,2H_2O,$$

forms garnet-red scales, and the corresponding *platinichloride*, $\{Fe[C_6H_4(FeO)O_7(NH_4)_2]_2(OH_2)_2\}\tfrac{1}{2}PtCl_6,3H_2O$, a reddish-brown, microcrystalline powder.

Diaquocitratoferrylcitrato-oldiamminodiferric citrate,

$$\left\{ Fe\begin{matrix}[C_6H_5O_7\cdot Fe(OH)] \\ [C_6H_4(FeO)O_7(NH_4)_2]\end{matrix}(OH_2)_2 \right\} \tfrac{1}{3}C_6H_5O_7,2H_2O,$$

forms large, reddish-brown scales, and the *platinichloride* a reddish-brown, microcrystalline powder.

Tricitratodiferric acid, $[Fe_2(C_6H_4O_7)_3]H_6$, forms yellowish-brown scales, and *trisodium* and *triammonium tricitratodiferriates*, $[Fe_2(C_6H_4O_7)_3](NH_4)_3H_3$, green scales.

Diammonium tricitratodiferriate, $[Fe_2(C_6H_4O_7)_3](NH_4)_2H_4$, is yellowish-green, and the *monoammonium* compound,

$$[Fe_2(C_6H_5O_7)_3](NH_4)H_5,$$

yellow; both are highly hygroscopic. T. H. P.

Aldol Condensation and Formation of Resin by the Action of Dilute Alkalis on Acetaldehyde. HARALD HAMMARSTEN (*Annalen*, 1920, **421**, 293—315).—In a previous paper (this vol., i, 710), the Cannizzaro reaction with acetaldehyde has been discussed, and the present communication deals mainly with the simultaneous formation of aldols and resin. The

naterials which have been examined are acetaldehyde and acetıldol, *acetone, and dimethylacetonylcarbinol*, $OH\cdot CMe_2\cdot CH_2\cdot COMe$, vhilst the bases are the hydroxides of potassium, lead, and barium .t 0°, 18°, and 50°. The estimation of acetaldehyde in the presence ıf aldol cannot be accurately performed by simple distillation of he mixtures, since the latter is sensibly decomposed before the ormer is quantitatively volatilised. A convenient method consists n drawing a rapid stream of purified air through the mixture at '5—30°/25—30 *mm.*; *acetaldehyde is thereby* volatilised, and is .bsorbed by a measured volume of *N*/5-iodine solution in the ıresence of *N*/1-potassium hydroxide, the excess of iodine being ubsequently titrated with *N*/10-thiosulphate. A molecule of acet-ıldehyde reacts with four atoms of iodine apparently in accord-nce with the equation $2Me\cdot CHO + 8I + 3KOH = 2CHI_3 +$ $I\cdot CO_2K + MeOH + 2KI + 2H_2O$. Acetaldehyde and aldol cannot e sufficiently sharply separated by extraction with ether, the espective partition coefficients between ether and water being ·15 and 0·66. The aldols cannot be estimated titrimetrically or olorimetrically, and they are therefore determined by first remov-ng the bulk of the resin by filtration of the solution, and then by ·xhaustive extraction with ether. The ethereal solution is dried, he solvent is removed at a low temperature, and the residue is veighed after being exposed to the action of phosphoric oxide at .tmospheric pressure during twenty-four hours. The aldols are ubsequently volatilised at 120°/10 mm., and any residual resin s weighed. The possibility of applying the magenta-sulphurous .cid colorimetric method to the estimation of aldols has been ·xamined, *and it is found that freshly distilled acetaldol gives a* oloration about 0·65 times as intense as that of an equivalent mount of acetaldehyde; the higher aldols, however, do not give coloration.

The results are given in a series of tables, for which the original ·aper must be consulted. It is shown that the chief reaction ·etween dilute acetaldehyde and alkalis consists in the formation f aldols, and that this occurs with hydroxyl-ion concentrations, /hich are as low as $2·5 \times 10^{-6}$ gram-ion per litre. The aldols are .ot utilised in subsequent reactions, such as formation of resin, ven when the temperature is raised and the time of contact pro-›nged. Acetaldol is the primary condensation product, but it apidly passes for the greater part into higher aldols, of which $OH\cdot CHMe\cdot[CH_2\cdot CH(OH)]_2\cdot CH_2\cdot CHO$ has been identified. Under he conditions adopted, less than 40% of aldols has never been btained from 0·5*N*-acetaldehyde solution. It appears, therefore, hat the more complex aldols cannot *yield aldehyde resin*, which s, however, produced from acetaldol.

The Cannizzaro reaction occurs far less rapidly than the aldol ondensation, but appears to be relatively more noticeable with ıore concentrated than with dilute solutions of potassium hydr-xide; with barium hydroxide, the influence of concentration is ·ss marked. Lead hydroxide is peculiar, since it induces neither

Cannizzaro's reaction nor resin formation, although production of aldol is fairly rapid. Temperature appears to have about the same catalysing action on all the changes, and the final equilibrium is therefore independent of this factor.

The constitution of aldehyde resin has been further investigated; for this purpose, aqueous solutions of acetaldehyde ($2N$) are allowed to remain for five to six days with an equal volume of aqueous potassium hydroxide solution (10%) at the ordinary temperature. The solution is exactly neutralised with hydrochloric acid, whereby the ordinary red resin, m. p. about 120° (decomp.) after softening from 96°, is precipitated, which is identical with the α- and β-aldehyde-resin described by Ekecrantz (A., 1912, i, 788). Further addition of a large volume of concentrated hydrochloric acid to the filtrate causes the separation of a very pale straw-yellow *resin*, which has m. p. 120—130° after softening at 105°, and commences to decompose above 200°. It appears to be a definite substance containing 66·13—66·73% C and 7·45—7·68% H, mol. wt. 396—412. The yellow resin appears to be first formed, since aldehyde solutions are initially coloured yellow by alkali and then clouded by the formation of a yellow precipitate, which darkens in colour as it increases in amount. It is uncertain whether the red resin is formed independently or through the yellow variety, but the former hypothesis is the more probable, since an alkaline solution of the yellow resin does not become turbid when preserved. The formation of aldehyde resin is not to be regarded as the final stage in the condensation of acetaldehyde; in solutions of the latter, the formation of acetate, ethyl alcohol, aldols, yellow and red resin, proceeds simultaneously.

Preliminary experiments with acetone indicate that, under the conditions adopted, an equilibrium is rapidly obtained between acetone and its condensation products in which not more than 14% of the former (at its boiling point) has undergone change. Complementary investigations with diacetone alcohol prove that this is a true equilibrium, and that this ketol is the main condensation product. H. W.

Process for the Purification of Acetone. J. Duclaux and A. Lanzenberg (*Bull. Soc. chim.*, 1920, [iv], 27, 779—782). —The process is based on the fact that acetone forms with carbon disulphide a mixture with a minimum boiling point of 39°. To the acetone, 1·7 times its volume of carbon disulphide is added, and the mixture is distilled, all that passes over between 38° and 40° being collected in three fractions. From these three fractions the acetone is extracted by water, and the aqueous extracts are distilled, the fraction boiling at 56·1—56·3° being collected. Methyl alcohol also forms a mixture with carbon disulphide which has b. p. 37·5°, and if this alcohol is present as an impurity in the acetone, the above process must be modified. The minimum b. p. distillate is left over potassium carbonate for some time before extraction with water, and copper sulphate is added to the aqueous

extract before its fractionation. In this way, most of the methyl alcohol is removed. W. G.

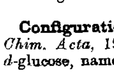
Researches on Residual Affinity and Co-ordination. II. Acetylacetones of Selenium and Tellurium. GILBERT T. MORGAN and HARRY DUGALD KEITH DREW (T., 1920, **117**, 1456—1465).

Preparation of Dihydroxyacetoxime. C. H. BOEHRINGER SOHN (D.R.-P. 322845; from *Chem. Zentr.*, 1920, iv, 437).—β-Nitropropylene glycol or one of its salts is treated with reducing agents in the presence of basic substances, such as the hydroxides of the alkalis or alkaline earths. Dihydroxyacetoxime,

$$OH{\cdot}N{:}C(CH_2{\cdot}OH)_2,$$

is almost quantitatively convertible into glycerol. H. W.

Constitution of Lævoglucosan. AMÉ PICTET and MARC CRAMER (*Helv. Chim. Acta*, 1920, **3**, 640—644).—Lævoglucosan, obtained by Tanret (A., 1894, i, 564) and by Vongerichten and Müller (A., 1906, i, 198) by hydrolysing certain glucosides, by Pictet and Sarasin (A., 1918, i, 59) by distilling cellulose or starch under reduced pressure, and by Karrer (this vol., i, 370) by distilling β-glucose in a vacuum, reacts with excess of acetyl chloride, giving β-acetochloroglucose (compare Skraup and Kremann, A., 1901, i, 506). When heated on a water-bath with neutral or faintly alkaline permanganate solution, lævoglucosan yields a syrupy compound, which does not reduce Fehling's solution, is neutral to litmus, reacts with phenylhydrazine, giving the *diphenylhydrazone*, $C_{18}H_{18}O_3N_4$, m. p. 154—155°, yields a basic, crystalline compound when treated with *o*-phenylenediamine, and is converted into a crystalline acetate by acetic anhydride. Formula I is attributed to this oxidation product and formula II to lævoglucosan itself. T. H. P.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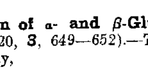
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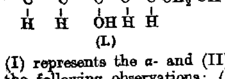
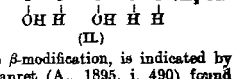
Configuration of α- and β-Glucoses. AMÉ PICTET (*Helv. Chim. Acta*, 1920, **3**, 649—652).—That, of the two formulæ for *d*-glucose, namely,


(I.)

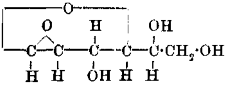
and


(II.)

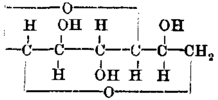
(I) represents the α- and (II) the β-modification, is indicated by the following observations: (1) Tanret (A., 1895, i, 490) found that, at 110°, α-glucose is slowly converted into the β-form; since

similar atoms or groups of atoms tend to repel one another, this transformation is more probably from (I) to (II) than from (II) to (I). (2) Böeseken (A., 1913, i, 1147) found that, in order that an alcohol may increase the electrical conductivity of boric acid solutions, it must possess at least two hydroxyl groups attached to two neighbouring carbon atoms and situate in the same plane and on the same side of the carbon atom chain; as α-glucose exhibits this property, it should have formula (I).

The accuracy of these indications is proved as follows by the author, the only assumption made being that the hydroxyls of glucose are able to react one with another, with loss of the elements of a molecule of water, only when such hydroxyls occur on the same side of the plane formed by the hydrofuran nucleus. With α-glucose there corresponds an anhydride, glucosan (compare Pictet and Castan, this vol., i, 594), which, having lost the hydroxyl groups attached to the first and second carbon atoms, possesses the grouping of an ethylene oxide, and can thus only have the structure (III). Lævoglucosan (preceding abstract), the anhydride of β-glucose, does not contain the primary alcoholic group of glucose, and corresponds with the configuration (IV). It is hence evident that α- and β-glucoses correspond, respectively, with formulæ I



(III.)



(IV.)

and II. The two anhydrides, differing so greatly in structure, are best termed, for the present, glucosan and lævoglucosan, and not, as suggested by Vongerichten and Müller (*loc. cit.*) and others, α- and β-glucosans. T. H. P.

The Influence of Different Substances on the Decomposition of Monoses by an Alkali and on the Inversion of Cane Sugar by Hydrochloric Acid. H. I. Waterman and J. Groot (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 149—161).—A study of the influence of *o*-phthalic acid, α- and β-naphthoic acids, cinnamic acid, *o*-coumaric acid, 1:2- and 2:3-hydroxynaphthoic acids, Schäffer salt, *G*-salt, and sodium phenol-*p*-sulphonate, respectively, on the decomposition of dextrose by alkali, and of the influence of 1:2- and 2:3-hydroxynaphthoic acids, cinnamic acid, *o*-coumaric acid, *o*-phthalic acid, α- and β-naphthol, and α-naphthoic acid, respectively, on the inversion of sucrose by hydrochloric acid. W. G.

Polysaccharides. I. Methylation of Starch. P. Karrer (*Helv. Chim. Acta*, 1920, **3**, 620—625).—The author has succeeded in methylating starch by treating it with methyl iodide and silver oxide in water, or with methyl sulphate and baryta water, etc. In

this way, three preparations have been obtained containing 1, about 1·5, and 2 *methoxyl groups, respectively*, per $C_6H_{10}O_5$. The first is readily soluble only in cold water, the second dissolves also *to some extent in alcohol*, and the third is readily soluble in water, alcohol, or chloroform. Fehling's solution is not reduced by any of these compounds or by the mother liquors from which they are obtained. With iodine they give, respectively, reddish-violet, brownish-yellow, and almost imperceptibly yellow colorations. Preliminary molecular-weight determinations of the third preparation indicate the value 1000—2000.

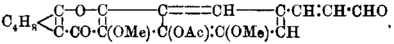
The author considers that the crystalloid starch can be broken down into molecules only when soluble derivatives are prepared, the process of dissolution effecting the depolymerisation. His view of the highly polymeric polysaccharides is to some extent similar to that of Hess and Wittelsbach (this vol., i, 532), but it should be unnecessary to employ a new name like "celluxose" to designate the true cellulose or starch molecule, such molecule differing from cellulose or starch only as a molecule does from a crystal (this vol., i, 370). T. H. P.

Lignin and Reactions of Lignin. II. PETER KLASON (*Ber.*, 1920, **53**, [*B*], 1862—1863. Compare this vol., i, 148, 474).—The author has previously described the isolation of the naphthylamine salt, $CH_2R\cdot CH<\begin{matrix}SO_2\text{-}O \\ CH:NH\cdot C_{10}H_7\end{matrix}$, *from* the lignin of the pine, and has now obtained similar compounds from fir, birch, beech, oak, linden, alder, and aspen, the composition of which, as indicated by estimation of nitrogen and sulphur, is practically the same in every case. Although the lignin of these different varieties is certainly not identical, it therefore appears that it invariably belongs to the same type. The lignin of herbaceous plants likewise yields yellow, cyclic arylammonium salts, but their composition differs considerably from that of those obtained from trees. H. W.

Constitution of Pine Lignin. PETER KLASON (*Ber.*, 1920, **53**, [*B*], 1864—1873).—The portion of lignin which contains an acraldehyde group, and in the form of its sulphonic acid yields cyclic arylammonium salts, is termed acraldehyde lignin or α-lignin; it is identical with the constituent that yields the calcium lignosulphonate precipitable by calcium chloride. The second lignin present in wood, the calcium sulphonate of which is not precipitable by calcium chloride, and does not give a cyclic salt, but contains a carboxyl group, is named carboxylignin or β-lignin.

The formula $C_{22}H_{22}O_7$ is deduced for α-lignin in the following manner. The author's analyses of calcium lignosulphonate give results in agreement with the formula $C_{40}H_{44}O_{18}S_2Ca$ [and thus harmonising with Hönig and Spitzer's analyses (A., 1918, i, 375) of the barium and calcium salts]; the lignin residue contained in the salt must thus have the composition $C_{20}H_{20}O_6$ or $C_{20}H_{22}O_6$, and since it is known that an acetyl group is removed from lignin

during treatment with the sulphite liquor, the original α-lignin must have the composition $C_{22}H_{22}O_7$, and this deduction is in harmony with the analyses of the cyclic naphthylamine salt. Lignin contains two methoxyl groups and one hydroxyl radicle, as is shown by methylation with methyl sulphate, but the latter is acetylated in α-lignin. The general behaviour of α-lignin is shown to be compatible with the conception of it as a flavone derivative, and the following formula is therefore suggested for it:



For β-lignin, the formula $C_{19}H_{18}O_9$ is deduced from the results of estimation of the ratio of α- to β-lignin in wood, of the proximate analysis of wood, and the composition of α-lignin. It can be converted into a calcium lignosulphonate, which contains the same number of atoms of calcium as of sulphur, and in which, therefore, a carboxyl group is present (presumably the group *CHR:CH·CHO* of α-lignin appears as CHR:CH·CO_2H in β-lignin). In the wood itself, the β-lignin is probably attached to a cellulose residue, and the compound is to be regarded as a direct product of assimilation, $19CH_2O = C_{19}H_{18}O_9 + 10H_2O$, rather than as a secondary compound produced from pre-formed cellulose (α-lignin is probably similar in its origin, $22CH_2O = C_{22}H_{22}O_7 + 11H_2O + 2O_2$).

The quantitative separation of α- and β-lignin can be effected by means of β-naphthylamine hydrochloride. The application of this process, combined with the proximate analysis of pine wood by 70% sulphuric acid, indicates in it the presence of carbohydrates (68%), lignin (30%), and other substances (2%), 63% of the lignin being present as the α-variety and 37% as the β-form. The fact that the two types of lignin are present in the very approximate molecular ratio 2:1 suggests that in all probability these substances are present in wood as a combination, of which the carboxyl group is further attached to the cellulose molecule; this mode of occurrence would thus present complete analogy with the tannins.

H. W.

The Alkylamines as Solvents. HOWARD MCKEE ELSEY (*J. Amer. Chem. Soc.*, 1920, **42**, 2080—2085).—The amines examined were mono-, di-, and tri-methylamines, ethylamine, propylamine, and *iso*propylamine in comparison with liquid ammonia. These amines were found to be fair solvents for many of the inorganic salts examined at the ordinary temperature. The solubilities have, however, high temperature-coefficients, and at the boiling point of liquid ammonia very few salts are perceptibly soluble in any of the amines. W. G.

Diethylenetriamine and Triethylenetetramine. ROBERT GEORGE FARGHER (T., 1920, **117**, 1351—1356).

Tetraethylammonium. HANS HEINRICH SCHLUBACH (*Ber.*, 1920, **53**, [*B*], 1689—1693).—In the hope of obtaining a stable

ammonium radicle, the author has electrolysed a solution of tetraethylammonium chloride in anhydrous liquid ammonia in a specially designed cell, which is so arranged as to exclude atmospheric air, the details of which are promised in a subsequent communication (compare McCoy and West, A., 1912, i, 539; Palmaer, A., 1903, i, 12). Dark blue streaks are immediately formed at the platinum cathode, and a dark bluish-black solution is ultimately obtained, which retains its colour during several hours at $-78°$. It exhibits strong absorption in the violet and red. When the solution is evaporated at about $-100°$, slow decomposition takes place, and the residue consists solely of unchanged chloride; at $-33°$, a mixture of tetraethylammonium chloride and triethylamine remains, showing that decomposition occurs according to the scheme $2NEt_4 = 2NEt_3 + C_4H_{10}$, and therefore in the same manner as with the simple ammonium radicle. The solution instantly reacts with iodine, giving tetraethylammonium iodide. If a current of dry oxygen is passed over the cathode, the blue streaks disappear immediately, and, after removal of the solvent, a pale yellow residue remains, which appears to contain very little of the tetraethylammonium peroxide (as would be expected from analogy with similar experiments with potassium salts), and to consist of unchanged chloride mixed with about 70% of tetraethylammonium hydroxide. The coloration is also discharged by acetylene, but a compound analogous to potassium acetylide does not appear to be formed. Tetramethyl- and tetra-*n*-propylammonium iodides behave similarly when subjected to electrolysis, but with phenyltriethylammonium iodide, diethylaniline immediately separates at the cathode. Attempts to obtain the free radicles by the action of potassium, sodium, or calcium on solutions of tetraalkylammonium salts in liquid ammonia have not been successful up to the present. The replacement of ammonia by pyridine or chloroform has not given satisfactory results. H. W.

Glycine and its Additive Compounds with Neutral Salts. HAROLD KING and ALBERT DONALD PALMER (*Biochem. J.*, 1920, **14**, 574—583).—In the main, the results of Pfeiffer and Modelski (A., 1912, i, 949; 1913, i, 709) regarding the definite nature of the compounds of glycine with calcium, barium, and strontium chlorides of the type $MCl_2,(C_2H_5O_2N)_2,H_2O$, and with lithium chloride and bromide of the types $LiCl$(or Br),$C_2H_5O_2N,H_2O$ and $LiCl$(or Br),$(C_2H_5O_2N)_2,H_2O$, are confirmed. Additive compounds with potassium haloids were not obtained, but with sodium bromide and iodide, compounds, $NaBr,(C_2H_5O_2N)_2,H_2O$, needles, and $NaI,(C_2H_5O_2N)_2,H_2O$, needles, were obtained. A compound with calcium iodide, $CaI_2,(C_2H_5O_2N)_2,3H_2O$, was isolated in the form of large, clear tablets.

Glycine usually crystallises in the monoclinic system, but when recrystallised from water it often separates in long needles or columns devoid of water of crystallisation. This is an unstable form, and gradually passes into the stable monoclinic form. The

purest stable glycine which the authors have prepared decomposes in the neighbourhood of 256° (uncorr.). There is progressive darkening from about 240° onwards.

The observations of Falk and Sugiura (A., 1918, i, 292) are not confirmed. J. C. D.

Behaviour of Glycine and its Allies on Electrochemical Oxidation. FR. FICHTER and MAX SCHMID (*Helv. Chim. Acta*, 1920, **3**, 704—714).—Electrolysis of a solution of glycine in *N*-sulphuric acid yields (1) a mixture of ammonia and various methylamines, the mixed chlorides of these being evidently what was regarded by Lilienfeld (A., 1904, i, 295) and by Kühling (A., 1905, i, 417) as ethylenediamine hydrochloride; (2) formic acid; (3) formaldehyde; and (4) carbon dioxide and monoxide. The initial reaction is expressed by the equation $NH_2 \cdot CH_2 \cdot CO_2H + O + 2 \text{ farads} = NH_3 + CH_2O + CO_2$. The heat generated at the anode then causes interaction of the formaldehyde and ammonia, a mixture of mono-, di-, and tri-methylamine being produced (compare Plöchl, A., 1888, 1051); a similar mixture of bases may, indeed, be obtained by electrolytic oxidation of a mixture of formaldehyde and ammonium sulphate solution. As the electrolysis proceeds, the yields of ammonia and carbon dioxide diminish, the former the more rapidly, owing to progressive oxidation of the formaldehyde; the final stage is represented by the equation

$$NH_2 \cdot CH_2 \cdot CO_2H + 3O + 6 \text{ farads} = NH_3 + 2CO_2 + H_2O.$$

Electrolysis of aqueous sodium acetylaminoacetate solution gives carbon dioxide in greater yields than, and ammonia in about the same yields as, with glycine; acetic acid, formaldehyde, and formic acid are detectable among the products. Similarly, iminodiacetic acid undergoes rapid and complete oxidation according to the equation $CO_2H \cdot CH_2 \cdot NH \cdot CH_2 \cdot CO_2H + 6O + 12 \text{ farads} = 4CO_2 + NH_3 + 2H_2O$. Methyliminodiacetic acid gives ammonia, methylamine, and carbon dioxide in good agreement with the equation

$$CO_2H \cdot CH_2 \cdot NMe \cdot CH_2 \cdot CO_2H + 6O + 12 \text{ farads} = NH_2Me + 4CO_2 + 2H_2O,$$

and with α-amino*iso*butyric acid the electrolysis corresponds with the equation $NH_2 \cdot CMe_2 \cdot CO_2H + O + 2 \text{ farads} = NH_3 + COMe_2 + CO_2$.

α-p-*Toluenesulphonylamino*iso*butyric acid*, $C_{11}H_{15}O_4NS$, prepared by the interaction of α-amino*iso*butyric acid and *p*-toluenesulphonyl chloride in alkaline solution, crystallises in long, white needles, m. p. 147°. α-*Benzenesulphonylamino*iso*butyric acid*, $C_{10}H_{13}O_4NS$, similarly prepared, forms white needles, m. p. 144°. α-*Benzenesulphonylmethylamino*iso*butyric acid*, $C_{11}H_{15}O_4NS$, prepared by treating the previous compound with methyl iodide and sodium hydroxide solution, crystallises in needles, m. p. 171°. When aqueous solutions of the sodium salts of the first and last of these three acids are electrolysed, both undergo profound oxidation, with liberation of sulphuric acid, which causes separation of the slightly soluble organic acid at the anode, and thus disturbs

the electrolysis. In the former case ammonia, and in the latter methylamine, is formed from the beginning in amounts corresponding with those of the carbon dioxide and sulphuric acid produced, so that here, too, the attack commences at the nitrogen atom.

With β-alanine, ammonia, carbon dioxide, acetic acid, and formaldehyde are produced, the ratio between carbon dioxide and ammonia indicating complete destruction of the carbon chain. Benzoyl-β-alanine, as sodium salt, is only slowly attacked on electrolysis, the darkening which occurs indicating removal and hydroxylation of the benzoyl group; ammonia appears immediately.

Electrochemical oxidation of the amino-acids may be compared with the oxidative desamination which these compounds undergo in the living organism, but is far more vigorous and profound. The results obtained show with certainty that Kolbe's synthesis cannot be effected with aliphatic amino-acids (compare A., 1918, i, 369). T. H. P.

The Methylation of Dipeptides. A. Kossel and S. Edlbacher (*Zeitsch. physiol. Chem.*, 1919, **107**, 45—51).—Glycylglycine hydrochloride was treated with methyl sulphate in the presence of sodium hydroxide. After two hours, the mixture was acidified with hydrochloric acid, evaporated to dryness under diminished pressure, and the residue then extracted with methyl alcohol in order to separate the sodium methyl sulphate; a colourless syrup was eventually obtained. The methylated product was precipitated as the picrate, from which it was afterwards liberated and crystallised from alcohol, m. p. 141°. The *aurichloride*, $C_7H_{14}O_3N_2,HAuCl_4$, melted at 155°. The *argentonitrate*,

$$C_7H_{14}O_3N_2,AgNO_3,$$

has m. p. 180°. The free base, on hydrolysis with sulphuric acid, yielded, amongst other products, glycine and betaine. The methylation of *dl*-alanylglycine was carried out in the same way as that of glycylglycine. The aurichloride, $C_8H_{16}O_4N_2,HAuCl_4$, obtained has m. p. 105°. On hydrolysis with sulphuric acid, glycine and *dl*-trimethyl-α-propiobetaine, m. p. 240°, were obtained. In both instances, three methyl groups were therefore introduced into the dipeptide. S. S. Z.

***d*-Glutamic Acid.** L. Hugounenq and G. Florence (*Bull. Soc. chim.*, 1920, [iv], **27**, 750—754).—*d*-Glutamic acid may best be isolated from its hydrochloride by evaporating the hydrochloride on a water-bath with an alcoholic solution of aniline, and extracting the residne with hot water. The glutamic acid separates on cooling. Calcium glutamate gives with calcium chloride a double salt, $C_{10}H_{16}O_8N_2Ca,CaCl_2,2H_2O$, $[\alpha]_D$ −2·25°. If a solution of the hydrochloride is saturated with freshly precipitated cupric hydroxide, a *copper* derivative, $(C_5H_9O_4N)_5,4CuO,7\frac{1}{2}H_2O$, is obtained as small, blue crystals. *Barium*, *zinc*, and *cadmium* salts of glutamic acid, and *mercury*, *cobalt*, and *nickel* derivatives, have been prepared. W. G.

The Direct Synthesis of Carbamide by Urease. H. P. BARENDRECHT (*Rec. trav. chim.*, 1920, **39**, 603—605).—A reply to Mattaar (this vol., i, 537). W. G.

The Constitution of Carbamides. XIII. The Constitution of Cyanic Acid, and the Formation of Urea from the Interaction of Ammonia and Cyanic Acid at Low Temperatures. EMIL ALPHONSE WERNER and WILLIAM ROBERT FEARON (T., 1920, **117**, 1356—1362).

The Interaction of Carbon Disulphide and Ammonium Carbonate. FRANÇOIS A. GILFILLAN (*J. Amer. Chem. Soc.*, 1920, **42**, 2072—2079).—Carbon disulphide and ammonium carbonate interact at 160°, giving a mixture of ammonium thiocyanate and thiocarbamide. The equilibrium depends on the concentration of the reagents used, the temperature and duration of heating, and the concentration of the hydrogen sulphide produced in the reaction. The yield of thiocarbamide is much below the theoretical value, and the method is not recommended. The reversion to ammonium thiocyanate is favoured by the presence of hydrogen sulphide.

The estimation of ammonium thiocyanate cannot be carried out accurately by the indirect titration method in a mixture containing more than 15% of thiocarbamide. Direct titration with silver nitrate, however, gives satisfactory results with mixtures containing as much as 40% of thiocarbamide. The interference is apparently due to the solubility of silver thiocyanate in thiocarbamide solutions.

In solutions containing not more than 5 mg. of thiocarbamide per 100 c.c., this substance may be estimated by titration with iodine. W. G.

Some Thiocyanates of Silver with Ammonium and Sodium. RADU CERNATESCU (*Bull. Acad. Sci. Roumaine*, 1920, **6**, 53—56). —The author has prepared two double thiocyanates of silver and sodium, NaCNS,AgCNS and 3NaCNS,AgCNS, and of silver and ammonium, NH_4CNS,AgCNS and $5NH_4CNS$,AgCNS. From the last salt, the silver is not precipitated by the addition of barium chloride. W. G.

New Synthesis of Hydrogen Cyanide by Catalysis. ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1920, [iv], **27**, 737—739).—When carbon monoxide and ammonia are passed together over thorium oxide at 410—450°, an excellent yield of ammonium cyanide is obtained. The thorium oxide may be replaced by aluminium oxide or zirconium oxides, but a higher temperature is then necessary. W. G.

A Sparingly Soluble Double Salt of Calcium Ferrocyanide and Calcium Ferrite. G. GRUBE [with L. BAUMEISTER and E. LÄMLE] (*Zeitsch. anorg. Chem.*, 1920, **112**, 245—261).—When Prussian-blue is decomposed with excess of calcium hydroxide into soluble calcium ferrocyanide and ferric

hydroxide, a side reaction occurs, the calcium ferrocyanide combining with the ferric hydroxide and excess of calcium hydroxide to form a sparingly soluble, white precipitate. As this is only stable in presence of excess of calcium hydroxide, and is decomposed by water, with formation of ferric hydroxide, it could not be isolated for analysis. By estimating the quantity of calcium ferrocyanide precipitated from solution by known quantities of ferric and calcium hydroxides, it was established that the constituents are present in the double salt in the proportion $Ca_2Fe(CN)_6:2Ca(OH)_2:4Fe(OH)_3$, and that the compound probably consists of a double salt of calcium ferrocyanide and calcium ferrite, $2CaFe_2O_4,Ca_2Fe(CN)_6$. The composition was confirmed by determinations of the change of hydroxyl-ion concentration in a calcium hydroxide solution caused by adding ferric hydroxide and calcium ferrocyanide. There is no evidence of the formation of calcium ferrite when ferric hydroxide is added to a saturated solution of calcium hydroxide. When calcium ferrocyanide is added to the mixture, the hydroxyl-ion concentration falls, and there is a break in the curve at the point corresponding with the composition $Ca_2Fe(CN)_6:2Ca(OH)_2:4Fe(OH)_3$. E. H. R.

Cyanoacetylene, C_3HN. CHARLES MOUREU and JACQUES CH. BONGRAND (*Ann. Chim.*, 1920, [ix], **14**, 47—58).—A more detailed account of work already published (A., 1911, i, 22). W. G.

Dicyanodimethyl Sulphide. WILHELM STEINKOPF (*Ber.*, 1920, **53**, [*B*], 1671).—The substance, described by Steinkopf, Herold, and Stöhr in their recent communication (this vol., i, 523), has been prepared previously and in a similar manner by von Zweigbergk (A., 1913, i, 24). H. W.

Carbon Subnitride, C_4N_2. CHARLES MOUREU and JACQUES CH. BONGRAND (*Ann. Chim.*, 1920, [ix], **14**, 5—47).—A more detailed account of work already published (compare A., 1910, i, 159; 1914, i, 671; this vol., i, 425). W. G.

The Freezing Point of Wet Benzene, and the Influence of Drying Agents. NEVIL VINCENT SIDGWICK (T., 1920, **117**, 1340—1343).

The System Benzene–Ethyl Alcohol–Water between +25° and −5°. NEVIL VINCENT SIDGWICK and WILLIAM JAMES SPURRELL (T., 1920, **117**, 1397—1404).

The Catalytic Action of Iodine in Sulphonation. I. JÑANENDRA NATH RÂY and MANIK LAL DEY (T., 1920, **117**, 1405—1407).

Use of Catalysts in the Sulphonation of Aromatic Compounds. JOSEPH A. AMBLER and WILLIAM J. COTTON (*J. Ind. Eng. Chem.*, 1920, **12**, 968—969).—The sulphonation of benzene in 70% sulphuric acid at 242—259° is accelerated by the addition of various catalysts in a concentration of 0·1% of the active element. The presence of compounds of the following elements slightly

increased the proportion of benzene sulphonated: copper, mercury, vanadium, chromium, potassium, and lithium, whilst a mixture of sodium sulphate and vanadium pentoxide had a pronounced effect. The catalytic action of sodium and potassium sulphates is not entirely due to their raising the boiling point of the sulphuric acid. The results indicated that members of the first group of the periodic system, represented by sodium and lithium, accelerated the formation of disulphonic acid, whilst the mixture of vanadium pentoxide and sodium sulphate was still more effective, but the other catalysts tried apparently inhibited the formation of that acid. C. A. M.

Preparation of certain Esters of Benzenesulphonic Acid. ZOLTÁN FÖLDI (*Ber.*, 1920, **53**, [*B*], 1836—1839).—The substances are conveniently prepared by the gradual addition of aqueous sodium hydroxide solution (20—30%) to a cold, well-stirred mixture of benzenesulphonyl chloride and the reqnisite alcohol until the mixture is permanently alkaline; the product is subsequently mechanically shaken for some hours, and the ester is ultimately distilled under diminished pressure. It is somewhat surprising to note tbat the method can be readily applied even with the halogenhydrins.

Allyl benzenesulphonate forms a colourless oil, D 1·166, which decomposes ultimately, with explosive violence, when distilled under diminished pressure. *β-Chloroethyl benzenesulphonate*, $SO_2Ph\cdot O\cdot CH_2\cdot CH_2Cl$, has b. p. 184°/9 mm., D_4^{15} 1·353, whilst the corresponding *bromo*-ester has b. p. 192°/20 mm., 185—187°/16 mm., D_4^{15} 1·575. *ββ′-Dichloro*iso*propyl benzenesulphonate*, $SO_2Ph\cdot O\cdot CH(CH_2Cl)_2$, long, colourless needles, m. p. 50°, b. p. 200—205°/20 mm., is very resistant towards hydrolysing agents.

In the case of β-chloroethyl benzenesulphonate, the benzenesulphonyl group is removed about four times as readily by alcoholic sodium hydroxide solution as is the chlorine atom, whilst in ββ′-dichloro*iso*propyl benzenesulphonate the chlorine atom is less firmly retained than the benzenesulphonyl radicle. H. W.

s-**Bromobenzenedisulphonic Acid.** S. C. J. OLIVIER and K. J. B. DE KLEERMAEKER, jun. (*Rec. trav. chim.*, 1920, **39**, 640—645. Compare Herzig, A., 1882, 46).—When bromobenzene is boiled with concentrated sulphuric acid under a reflux condenser for eight hours, 5-bromobenzene-1:3-disulphonic acid is obtained, which gives a *disulphonyl chloride*, m. p. 99—100°, a *diamide*, m. p. 255—256°, and *barium*, *potassium*, and *lead* salts. The disulphonyl chloride, when heated with phosphorus pentachloride, yields *s*-trichlorobenzene. W. G.

Possible Influence of Electronegative Groups on the Mobility of the Methylene Hydrogen Atoms in Arylsulphonated Methylene Derivatives. J. TRÖGER and E. NOLTE (*J. pr. Chem.*, 1920, [ii], **101**, 136—157. Compare Tröger and Vasteling, A., 1905, i, 870; Tröger and Beck, A., 1913, i, 630; Tröger and Wunderlich, A., 1915, i, 792).—It is found that the

methylene hydrogen atoms are not mobile in sulphones of the general formula $X\cdot C_6H_4\cdot SO_2\cdot CH_2Ph$ or $X\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot C_6H_4X$ (in which X is a nitro- or hydroxyl group or a halogen atom). Apparently the substituents are too far removed to exert an effect on the methylene group; when, however, they are brought nearer, as in compounds of the type $R\cdot SO_2\cdot CH_2\cdot NO_2$ and $R\cdot SO_2\cdot CH_2\cdot CN$, the resulting substances are soluble in alkali and readily undergo condensation.

Benzenesulphonyl-m-*nitrophenylmethane*, $SO_2Ph\cdot CH_2\cdot C_6H_4\cdot NO_2$, is prepared by the action of *m*-nitrobenzyl chloride on sodium benzenesulphinate in boiling alcoholic solution; it forms colourless, shining needles, m. p. 163°, whilst the corresponding o- and p-*derivatives* consist of colourless needles, m. p. 113°, and crystalline crusts, m. p. 207°, respectively. The isomerides are insoluble in aqueous sodium hydroxide solution (15%); attempts to methylate the *ortho*-compound by methyl iodide and sodium ethoxide at 100°, or to bring it into action with benzenediazonium chloride, were unsuccessful. Reduction with tin and fuming hydrochloric acid transforms the nitro-compounds into the corresponding amino-*derivatives*, of which the *o*-isomeride forms discoloured needles, m. p. 174° (*hydrochloride*, irregular leaflets), the *m*-base crystallises in coarse, pale brown needles, m. p. 139° (*hydrochloride*, colourless needles grouped to aggregates), and the *p*-isomeride (previously described by Hinsberg and Himmelschein as aminotolylphenylsulphone) has m. p. 176°; attempts to methylate the latter by methyl iodide and sodium ethoxide at 100° were completely unsuccessful, and did not even affect the free amino-group. Benzenesulphonyl-*m*-aminophenylmethane is converted in the usual manner into *benzenesulphonyl*-m-*hydroxyphenylmethane*, small, discoloured needles, m. p. 125°, which is converted by an excess of methyl iodide and sodium ethoxide at 100° into *benzenesulphonyl*-m-*methoxyphenylmethane*, yellowish-white leaflets, m. p. 109°.

Attempts are described to prepare *benzenesulphonylnitromethane*, $SO_2Ph\cdot CH_2\cdot NO_2$, by the action of chloronitromethane on sodium benzenesulphinate in the presence of a little alcohol, but grave difficulties are caused by the acidic nature of the latter, and the yields are very poor; the products are partly soluble and partly insoluble in sodium hydroxide solution, and, from the former, two *substances*, colourless crystals, m. p. 151° and m. p. 69—72°, respectively, have been isolated, which give analytical results in agreement with those required by benzenesulphonylnitromethane. The substance of lower m. p. reacts with benzenediazonium chloride to yield a reddish-yellow, crystalline product, which is either a hydrazone or an azo-compound, and the formation of which demonstrates the mobility of the hydrogen atoms of the parent substance. Somewhat better results are obtained when the reaction is applied to sodium *p*-bromobenzenesulphinate; in this instance, p-*bromobenzenesulphonylnitromethane* is isolated in colourless, shining needles, m. p. 161°, although the yields are

poor. The substance dissolves in aqueous sodium hydroxide solution, and with benzenediazonium chloride gives a *product*, golden-yellow needles, m. p. 164°, which is probably to be regarded as the hydrazone, $C_6H_4Br\cdot SO_2\cdot C(:N\cdot NHPh)\cdot NO_2$, since it dissolves in cold sodium hydroxide solution to form a *sodium* salt, thin, yellow needles.

The following substances were prepared from their components with the object of investigating the conjoint influence of a halogen atom in the phenylsulphonyl group and a nitro-group in the phenyl radicle attached to the methylene group: p-*chlorobenzenesulphonyl*-p-*nitrophenylmethane*, $C_6H_4Cl\cdot SO_2\cdot CH_2\cdot C_6H_4\cdot NO_2$, colourless needles, m. p. 162°; p-*chlorobenzenesulphonyl*-m-*nitrophenylmethane*, shining leaflets, m. p. 179°; p-*chlorobenzenesulphonyl*-o-*nitrophenylmethane*, yellowish-white, irregular crystals, m. p. 137°; p-*bromobenzenesulphonyl*-o-*nitrophenylmethane*, plates, m. p. 137°; p-*bromobenzenesulphonyl*-m-*nitrophenylmethane*, colourless, crystalline powder, m. p. 182°; p-*bromobenzenesulphonyl*-p-*nitrophenylmethane*, microcrystalline powder, m. p. 195°; p-*iodobenzenesulphonyl*-o-*nitrophenylmethane*, small, colourless leaflets, m. p. 129°; p-*iodobenzenesulphonyl*-m-*nitrophenylmethane*, colourless, shining needles, m. p. 218°; p-*iodobenzenesulphonyl*-p-*nitrophenylmethane*, brownish-yellow needles, m. p. 223·5°. Certain of these have been reduced by tin and fuming hydrochloric acid in glacial acetic acid solution, yielding thereby: p-*bromobenzenesulphonyl*-p-*aminophenylmethane*, pale yellow needles, m. p. 187° (*hydrochloride*, silvery crystals); p-*bromobenzenesulphonyl*-m-*aminophenylmethane*, leaflets, m. p. 146° (*hydrochloride*, silvery crystals); p-*bromobenzenesulphonyl*-o-*aminophenylmethane*, leaflets (*hydrochloride*, coarse, prismatic, yellow needles). p-*Bromobenzenesulphonyl*-p-*hydroxyphenylmethane*, yellowish-white, uncharacteristic crystals, m. p. 194·5°, is obtained by the diazotisation of the corresponding amine at 60—70° under pressure, and subsequent heating of the diazonium solution; its solubility in sodium hydroxide solution appears to be due solely to the presence of the phenolic hydroxyl group.

p-*Toluenesulphonyl*-m-*nitrophenylmethane* forms colourless octahedra, m. p. 162°, whilst the corresponding *o*- and *p*-nitrophenyl *derivatives* crystallise in yellowish-white needles, m. p. 132°, and small, colourless, shining needles, m. p. 182°, respectively.

The effect of the presence of a nitro-group in the arylsulphonyl radicle has been investigated at the instance of the following compounds: *p*-nitrophenylbenzylsulphone, m. p. 169°, obtained by the oxidation of *p*-nitrophenyl benzyl sulphide by permanganate, which, contrary to the observations of Fromm and Wittmann (A., 1908, i, 631), is not methylated by treatment with methyl iodide and sodium ethoxide at 100°; m-*nitrobenzenesulphonylphenylmethane*, yellowish-white, silky needles, m. p. 160° (m-*aminobenzenesulphonylphenylmethane*, colourless, pointed needles, m. p. 119·5°); m-*nitrobenzenesulphonyl*-p-*nitrophenylmethane*, brown platelets, m. p. 192°; m-*nitrobenzenesulphonyl*-o-*nitrophenyl*-

methane, brown crystals, m. p. 184°; m-*nitrobenzenesulphonyl*-m-*nitrophenylmethane*, yellowish-white needles, m. p. 171°.

m-*Nitrobenzenesulphonylacetonitrile*, $NO_2\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot CN$, is obtained with unexpected difficulty and in poor yield by the action of chloroacetonitrile on sodium *m*-nitrobenzenesulphinate at 130°; the mobility of its methylene hydrogen atoms is proved by its solubility in aqueous alkali, its power to condense with aldehydes to form substances, such as m-*nitrobenzenesulphonylanisylideneacetonitrile*, $NO_2\cdot C_6H_4\cdot SO_2\cdot C[:CH\cdot C_6H_4(OMe)]\cdot CN$, pale yellow, silky needles, m. p. 160°, and its ability to react with benzenediazonium chloride to give m-*nitrobenzenesulphonylbenzeneazoacetonitrile* (or the *phenylhydrazone* of m-*nitrobenzenesulphonylformyl cyanide*), reddish-yellow needles, m. p. 175°, which form salts with bases. H. W.

Modification and Extension of the Friedel and Crafts' Reaction. I. Jnanendra Nath Rây (T., 1920, **117**, 1335—1339).

Organic Molecular Compounds. II. James F. Norris and Dorothy M. Tibbetts (*J. Amer. Chem. Soc.*, 1920, **42**, 2085—2092).—It has been shown that tetraphenyldichloroethane forms well-characterised molecular compounds with chloroform and carbon tetrachloride (A., 1911, i, 31), and later that other organic compounds of certain types, such as tetra-*p*-bromophenylethylene, possesses to a high degree the power to form molecular compounds (A., 1916, i, 380). The authors propound the following hypothesis in explanation. The molecular compound is formed as a result of the coming into play of latent affinities residing on an atom in each of the constituents of the compound. All atoms possess these latent affinities, but whether or not they are of such a nature as to permit the union of a molecule with a second molecule is determined by the extent to which the chemical energy of the atom in question has been expended in the formation of the molecule containing it. In the case of unsaturated compounds containing a double linking, the molecular compounds are most often formed by direct addition, but sometimes their formation is due only to the latent chemical affinity of the double bond.

In addition to the molecular compounds previously described, it is now shown that tetra-*p*-bromophenylethylene forms well-crystallised molecular compounds with toluene, *p*-xylene, chlorobenzene, ethyl ether, ethyl and propyl acetates, and ethyl propionate, but not with chloroform, ethyl or amyl alcohol, bromo- or iodo-benzene, *m*-xylene, light petroleum, methyl acetate, or ethyl formate. This method may therefore be employed in separating ethyl alcohol from acetone and *p*-xylene from *m*-xylene. If the bromine is replaced by chlorine, the ability to form molecular compounds is much reduced. Tetra-*p*-chlorophenylethylene only formed additive products with benzene, carbon tetrachloride, and methyl ethyl ketone.

Triphenyl-*p*-chlorophenylethylene only formed a molecular com-

pound with carbon tetrachloride, and tetraphenylethylene did not give any molecular compounds. It should be noted that whereas triphenylchloromethane forms molecular compounds, the corresponding bromo-derivative does not.

Triphenylchloromethane and triphenylcarbinol both give molecular compounds, but the corresponding diphenyl compounds do not. On the other hand, *p*-phenyldiphenylcarbinol,

$C_6H_4Ph \cdot CHPh \cdot OH$,

and *p*-phenyldiphenylchloromethane, $C_6H_4Ph \cdot CHPhCl$, both yield molecular compounds with carbon tetrachloride. *p*-Bromodiphenylcarbinol and di-*p*-chlorophenylcarbinol did not give molecular compounds. W. G.

Relationship of Retene to the Resin Acids, Hydrogenated Retenes. ARTTURI J. VIRTANEN (*Ber.*, 1920, **53**, [*B*], 1880—1889).—A considerable number of hydrogenated retenes have been prepared with the ultimate object of elucidating their relationship to the resin acids, the literature of which is exhaustively reviewed. With the exception of tetrahydroretene, the substances are stable towards permanganate, which is rather surprising, in view of the fact that some of them, at any rate, are unsaturated. Attempts to prepare picrates of the hydrocarbons were unsuccessful in every case.

Dihydroretene, $C_{18}H_{20}$, colourless, shining leaflets, m. p. 64—65°, b. p. 188—190°/10 mm., is obtained by the action of sodium on a boiling solution of retene in amyl alcohol; it is oxidised by chromic acid in glacial acetic acid solution to retenequinone. Tetrahydroretene, prepared in a similar manner, but with a larger proportion of sodium, is a yellow oil with a peculiar, very unpleasant odour, b. p. 180—183°/10 mm., D_4^{20} 1·0057, n_D^{20} 1·56061. The more highly hydrogenated retenes are obtained from the parent hydrocarbon, fuming hydriodic acid (D 1·96), and red phosphorus under varied conditions of temperature and relative proportions of reagents; *hexahydroretene*, colourless oil, b. p. 175—177°/10 mm., D_4^{20} 0·9802, n_D^{20} 1·54705; *octahydroretene*, colourless oil, b. p. 163—165°/10 mm., D_4^{20} 0·9578, n_D^{20} 1·53023; decahydroretene, colourless oil, b. p. 155—158°/10 mm., D_4^{20} 0·9342, n_D^{20} 1·51501; and *dodecahydroretene*, colourless oil, b. p. 148—150°/10 mm., D_4^{20} 0·8985, n_D^{20} 1·48510, are described. Tetra-, hexa-, octa-, and deca-hydroretenes appear to be nitrated by warm concentrated nitric acid, towards which the dodeca-compound is stable.

H. W.

Geometrical Isomerism of Polymethylenes. A. SKITA (*Ber.*, 1920, **53**, [*B*], 1792—1806).—In general, chemical methods for the preparation of the various stereoisomeric derivatives of *cyclo*hexane are at present unknown, and it is not possible to obtain any selected stereoisomeride at will from a definite initial material. Since the recent investigations of von Auwers (*A.*, 1919, i, 578) have afforded trustworthy physical methods of placing

isomerides in the *cis*- or *trans*-series, it appeared desirable to apply a number of different methods to the reduction of the same unsaturated substance with the object of classifying the processes in accordance with their tendency to produce *cis*- or *trans*-isomerides. For this purpose, 2:4:5-trimethylaniline has been selected. It is reduced by hydrogen in the presence of colloidal platinum in strongly acid solution to 2:4:5-trimethyl*cyclo*hexylamine; on the other hand, it is converted by nitrous acid into 2:4:5-trimethylphenol, which is similarly reduced to 2:4:5-trimethyl*cyclo*hexanol (the corresponding hydrocarbon and ketone are also described), which differs from the similar series obtained by Auwers (this vol., i, 721) from 2:4:5-trimethylphenol by Sabatier's process in that the individual members have relatively greater density and index of refraction and smaller molecular refraction, and are therefore characterised as *cis*-compounds, whilst those described by von Auwers belong to the *trans*-series. The oxime of the author's *cis*-1:2:4-trimethyl*cyclo*hexane-5-one is reduced in acid solution to the amine, obtained from ψ-cumidine (which is thus also a *cis*-compound), but with sodium and alcohol it gives an isomeric base, which is regarded as *trans*-5-amino-*cis*-1:2:4-trimethyl*cyclo*hexane. Similarly, 1:2:4-trimethyl*cyclo*hexane-5-one yields *trans*-5-hydroxy-*cis*-1:2:4-trimethyl*cyclo*hexane in acid solution, and *trans*-5-hydroxy-*cis*-1:2:4-trimethyl*cyclo*hexane in alkaline solution; the former is identical with the product obtained by the catalytic hydrogenation of ψ-cumenol in acetic acid solution in the presence of colloidal platinum, but the latter differs from the product prepared by Sabatier's process, which is to be regarded as 5-hydroxy-*trans*-1:2:4-trimethyl*cyclo*hexane.

It therefore appears justifiable to conclude that reduction of double bonds in acid solution favours the production of *cis*-forms, whilst *trans*-varieties are preferentially obtained in alkaline or neutral media; this generalisation, however, has only been tested up to the present for hydrocarbons, alcohols, and amines.

[With WILHELM HENNENBRUCH.]—The following substances are described: 1:2:4-*trimethyl*cyclo*hexane*, b. p. 33°/11 mm., 144·8—145·8° (corr.)/760 mm., D_4^{20} 0·790, n_D^{20} 1·434; cis-5-*hydroxy*-cis-1:2:4-*trimethyl*cyclo*hexane*, b. p. 84°/17 mm., 191—193° (corr.)/760 mm., D_4^{20} 0·912, n_D^{20} 1·463 (*phenylurethane*, m. p. 83·5°); cis-1:2:4-*trimethyl*cyclo*hexane-5-one*, b. p. 193° (corr.), D_4^{20} 0·905, n_D^{20} 1·450 (*semicarbazone*, needles, m. p. 204°; *oxime*, m. p. 105°); trans-5-*hydroxy*cis-1:2:4-*trimethyl*cyclo*hexane*, b. p. 112°/35 mm., 196° (corr.)/760 mm., D_4^{20} 0·906, n_D^{20} 1·461 (*phenylurethane*, m. p. 95°; *hydrogen phthalate*, m. p. 81—83·5°). cis-5-*Amino*-cis-1:2:4-*trimethyl*cyclo*hexane*, from 1:2:4-trimethyl-5-*cyclo*hexylamine, or *cis*-1:2:4-trimethyl*cyclo*hexane-5-one oxime in acid solution by sodium amalgam or hydrogen and colloidal platinum, b. p. 74°/17 mm., 188—190° (corr.)/760 mm., D_4^{20} 0·864, n_D^{20} 1·462 (*picrate*, m. p. 212° after softening at 208°; *hydrochloride*, m. p. 227—228°; d-α-*bromocamphor*-π-*sulphonate*, colourless needles, m. p. 171·5°; *acetyl* derivative, needles, m. p. 100°;

benzoyl derivative, m. p. 107·5—108°; *phenylcarbamide*, oil; *phenylthiocarbamide*, needles, m. p. 164°); trans-5-*amino*-cis-1:2:4-*trimethyl*cyclo*hexane*, m. p. 21°, b. p. 187—188°/760 mm., D_4^{20} 0·857, n_D^{20} 1·458 (*hydrochloride*, decomp. 260°; d-α-*bromocamphor-π-sulphonate*, decomp. 205—210°; *benzoyl* derivative, needles, m. p. 174·5°; *phenylcarbamide*, needles, m. p. 169°; *phenylthiocarbamide*, m. p. 155°); trans-5-*hydroxy*-cis-1:2:4-*trimethyl*cyclo*hexane*, formed, together with small amounts of 1:2:5-*trimethyl*cyclo*hexene*, b. p. 149° (corr.), by the action of sodium nitrite on the corresponding amine hydrochloride, b. p. 196° (corr.)/760 mm., D_4^{20} 0·906, n_D^{20} 1·461 (*phenylurethane*, m. p. 95°; *hydrogen phthalate*, m. p. 81—83°); cis-5-*amino*-cis-trans-1:2:4-*trimethyl*cyclo*hexane*, obtained as by-product of the catalytic hydrogenation of 2:4:5-trimethylaniline, b. p. 181—182° (*picrate*, m. p. 153°; phenylthiocarbamide, m. p. 110°). H. W.

Some Physical Constants of Pure Aniline. C. L. Knowles (*J. Ind. Eng. Chem.*, 1920, **12**, 881—883).—Aniline solidifies at −6·24°, and has b. p. 184·32—184·39°/760 mm., D_{15}^{15} 1·0268, n_D^{20} 1·5850. The solidifying point appears to be the best criterion of the purity of aniline, and this constant may be used as a basis for the estimation of actual aniline in a sample. The impurities most frequently found in commercial aniline are nitrobenzene, toluidine, and water; assuming the average molecular weight of these impurities to be 82·67, the percentage (X) of aniline is found by the formula $X = 108·79 + 1·41t$, where t is the observed solidifying point. W. P. S.

Crystalline Form of 2:4-Dibromo-3-nitroacetanilide. Maria De Angelis (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 47—53. Compare this vol., i, 608).—This compound is not isomorphous with the corresponding dichloro-compound, but forms crystals, D 2·131, belonging to the pinacoidal class of the triclinic system, $a : b : c = 1·2526 : 1 : 1·0013$, $\alpha = 96°54'$, $\beta = 104°39'$, $\gamma = 108°35'$. Mixtures of the dichloro- and the dibromo-compounds form monoclinic crystals completely isomorphous with those of the β-modification of the dichloro-derivative. T. H. P.

Some Condensation Products of Aromatic Aldehydes and Amines. F. M. Jaeger (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 74—83).—With a view of studying the polymorphism or isomerism of Schiff's bases, the author has prepared the following compounds and studied their crystallographic and optical properties.

o-Hydroxy-*m*-methylbenzylideneaniline (compare Anselmino, A., 1906, i, 13; 1907, i, 913) is obtained in red, monoclinic, prismatic crystals, $a : b : c = 0·2362 : 1 : 0·6579$, $\beta = 74°9\frac{1}{2}'$, D_4^{17} 1·263, m. p. 74°, and in yellow (metastable), rhombic-bipyramidal crystals, $a : b : c = 0·3732 : 1 : 0·4228$, D_4^{17} 1·243, m. p. 70°. By the action of methyl sulphate, it yields *o-methoxy-m-methylbenzylideneaniline*, m. p.

70°, pale yellow, monoclinic-prismatic crystals, $a:b:c=1\cdot2792:1:1\cdot0509$, $\beta=76°59\frac{1}{3}'$, D_4^{18} 1·166. When acted on with magnesium methyl iodide, it gives *o-hydroxy-m-methyl-α-anilino-ethylbenzene*, $OH\cdot C_6H_3Me\cdot CHMe\cdot NHPh$, m. p. 90°, monoclinic-prismatic crystals, $a:b:c=0\cdot2682:1:0\cdot7254$, $\beta=85°47'$, D_4^{17} 1·107. *o-Methoxy-m-methyl-α-anilinoethylbenzene*, m. p. 78°, gives rhombic-bipyramidal crystals, $a:b=0\cdot3301:1$, D_4^{16} 1·098. *o*-Hydroxybenzylideneaniline, m. p. 50·5° (compare Duparc, *Annalen*, 1891, **266**, 140), occurs in two forms, α-form, rhombic-bipyramidal crystals, $a:b:c=0\cdot4729:1:0\cdot2188$, D_4^{16} 1·087; β-form, monoclinic-prismatic crystals, $a:b=2\cdot4641:1$, $\beta=26°2\frac{1}{2}'$, D_4^{17} 1·184. On methylation, it gives *α-anilinoethylanisole*, m. p. 46°, rhombic-bipyramidal crystals, $a:b:c=0\cdot884:1:0\cdot465$, D_4^{18} 1·141. *p-Methoxybenzylideneaniline*, m. p. 63°, occurs in monoclinic-prismatic crystals, $a:b:c=1\cdot5745:1:0\cdot8063$, $\beta=65°21'$, D_4^{17} 1·165. W. G.

Action of Aluminium Chloride on Solutions of Aromatic Nitrohydrocarbons in Aromatic Hydrocarbons. A. Kliegl and Hans Huber (*Ber.*, 1920, **53**, [*B*], 1646—1655).—It has been shown by Freund that *p*-aminodiphenyl, in addition to much resinous matter, is formed when aluminium chloride acts on a boiling solution of nitrobenzene in benzene. In the hope of obtaining further insight into the action, the authors have repeated Freund's experiments, with the substitution of toluene for benzene, and have thus obtained *p*-aminophenyl-*p*-tolyl, which differs, however, from the similarly named substance prepared independently by Bamberger (A., 1895, i, 289) and Kühling (A., 1895, i, 182); the latter compound is shown to be *p*-aminophenyl-*o*-tolyl. The mechanism of the reaction is not yet fully elucidated, but progress has been made by the isolation of *N*-phenyl-*p*-toluidine as a by-product; it therefore appears that β-phenylhydroxylamine is intermediately formed, which in part condenses immediately, in part after transformation to *p*-aminophenol (or at the instant of transformation), with the aromatic hydrocarbon, with elimination of water: $NHPh\cdot OH+C_6H_5Me=C_6H_5\cdot NH\cdot C_6H_4Me+H_2O$ and $NH_2\cdot C_6H_4\cdot OH+C_6H_5Me=NH_2\cdot C_6H_4\cdot C_6H_4Me+H_2O$. It is definitely proved that *N*-phenyl-*p*-toluidine and *p*-aminophenyl-*p*-tolyl are formed when a solution of β-phenylhydroxylamine in toluene is treated with aluminium chloride, but, on the other hand, pre-formed *p*-aminophenol is not condensed with aromatic hydrocarbons by aluminium chloride, with formation of *p*-aminodiphenyls. It therefore appears that, at the instant at which the hydrogen atom and the hydroxyl group in β-phenylhydroxylamine leave their positions in the primary stage of the transformation, the aromatic hydrocarbon attaches itself to the free valency of the residual molecule.

Anhydrous aluminium chloride is gradually added to a boiling mixture of nitrobenzene and toluene; the product is poured into water, and unused materials are removed in a current of steam. The aqueous solution is filtered from resin and cooled, whereby

p-*aminophenyl*-p-*tolyl hydrochloride* is deposited in silvery leafl which rapidly become discoloured; the free *base* forms colour crystals, m. p. 99°, b. p. 190°/18 mm. (*acetyl* derivative, colc less crystals, m. p. 221°). The residues from the condensati when treated with superheated steam, give a small amount *N*-phenyl-*p*-toluidine, slender, colourless needles, m. p. 88—8 p-*Hydroxyphenyl*-p-*tolyl*, silvery leaflets, m. p. 154—155° (*ben* derivative, colourless, shining leaflets, m. p. 188°), is prepared the diazotisation of the base described above, and treatment of diazonium salt with water. The same phenol is obtained fi diazotised *p*-toluidine and phenol by Hirsch's method (D.R 58001), whilst *o*-toluidine, under similar treatment, gives *p*-hy oxyphenyl-*o*-tolyl, slender, colourless needles, m. p. 84— (*benzoyl* derivative, colourless needles, m. p. 89°), which is ident with the product obtained from Bamberger's base. The pc position of the methyl group in the authors' base is thus definit established, whilst the position of the amino-group (and hence the hydroxy-group in the phenol) follows from the analogous p duction of *p*-aminodiphenyl and from the identity of the base w that obtained by reduction of the product obtained by nitrat 4-methyldiphenyl. The latter substance, colourless leaflets, m. 49—50°, is obtained by the action of nitrosoacet-*p*-toluidide benzene.

4-*Amino*-3:4'-*dimethyldiphenyl*, m. p. 42—43°, is obtained fr *o*-nitrotoluene and toluene; the *acetyl* derivative crystallises colourless needles, m. p. 206°. H. W

Manufacture of 4-Nitro-β-naphthol. GILBERT THO MORGAN and BRITISH DYESTUFFS CORPORATION, LTD. (Brit. P 152437).—2:4-Dinitro-α-naphthylamine, which may be obtained the action of alcoholic ammonia at 220° on 2:4-dinitro-α-naphtl or by the nitration and subsequent hydrolysis of aceto-α-naph alide, is treated with nitrosyl sulphate or sodium nitrite in c centrated sulphuric acid, and the solution added to water precipitate 4-nitronaphthalene-1-diazo-2-oxide. On warming t diazo-oxide with ethyl alcohol, either alone or in presence of metallic catalyst, such as zinc, copper, aluminium, or a zinc–copj couple, or of a reducing agent, such as hypophosphorous acid, it converted into 4-nitro-β-naphthol, which is purified by extracti with hot water, from which it crystallises in yellow needles, m. 120°. 4-Nitro-β-naphthol couples with the diazo-derivatives substances such as sulphanilic acid, *p*-nitroaniline, safranine, a dianisidine, giving azo-compounds, which are of value as dyes cotton, wool, and silk. G. F. M

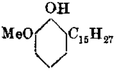
Manufacture of Anthranol. ARTHUR GEORGE PERKIN (B Pat. 151707).—Anthranol is obtained by heating anthraquinc (60 parts) with dextrose (60 parts), and a 30% solution of sodi hydroxide (650 parts), in an autoclave provided with stirring ge at 230° for five to ten hours. The product is then precipital from the reaction mixture by the addition of hydrochloric a

or by leading in carbon dioxide. Instead of dextrose in this reaction, sucrose, molasses, maltose, lactose, and the like may be used with similar results. G. F. M.

The Determination of the Configuration of Cyclic *cis*- and *trans*-Diols and the Rearrangements of Atoms and Groups of Atoms during Chemical Reactions. J. Böeseken and Chr. van Loon (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 69—73).—The effect of stereoisomeric diols on the conductivity of boric acid, or their behaviour on condensation with an active carbimide, or on condensation with acetone, may be used as a means of distinguishing between the *cis*- and *trans*-forms. As a rule, the *cis*-form augments the conductivity of boric acid, yields only one urethane, and readily yields a condensation product with acetone. In this way, the authors show that *cis*-hydrindenediol has m. p. 108°, *cis*-*cyclo*pentanediol has m. p. 29—30°, and that, contrary to the statement of Brunel, the *cis*-form of *cyclo*hexanediol is apparently the one having m. p. 99°. The method of preparation of diols by the oxidation of *cyclo*pentene or *cyclo*hexene appears to yield in each case the *cis*-form. W. G.

Derivatives of Phenyldihydroresorcin. Alexander John Boyd, Percy Herbert Clifford, and Maurice Ernest Probert (T., 1920, **117**, 1383—1390).

The Main Constituent of Japanese Lac. VII. Urushiol Monomethyl Ether and the Mechanism of the Oxidation of Urushiol. Rikō Majima and Gitaro Takayama (*Ber.*, 1920, **53**, [*B*], 1907—1916. Compare A., 1916, i, 38, and previous abstracts).—One of the two hydroxyl groups of urushiol is more readily methylated than the other, and the compound obtained by partial methylation is shown by a comparison of the properties of its tetrahydro-derivative with those of 2-hydroxy-*m*-tolyl methyl ether (Majima and Okazaki, A., 1916, i, 808) to be 2-hydroxy-3-methoxyurushiol (annexed formula). The tolyl derivative is shown to be oxidisable to a series of derivatives of diphenoquinone, and as precisely similar phenomena are observed during the oxidation of hydrourushiol, it appears valid to conclude that analogously constituted products are also formed in this case.



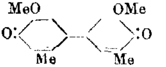
Urushiol is heated with sodium ethoxide and methyl sulphate in ethyl-alcoholic solution, and the *monomethyl ether* is separated from unchanged material and the dimethyl ether by fractional distillation under greatly reduced pressure; the slightly impure product is catalytically reduced by hydrogen in the presence of platinum to *hydrourushiol monomethyl ether*,

$$OMe{\cdot}C_6H_3(OH){\cdot}C_{15}H_{31},$$

colourless needles, m. p. 44·5—45°, which is also obtainable by the partial hydrolysis of hydrourushiol dimethyl ether with

hydriodic acid (D 1·7). *Hydrourushiol monomethyl ether acetate* crystallises in colourless leaflets, m. p. 45·5—46·5°.

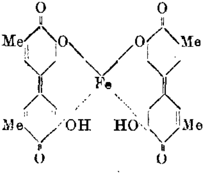
2-Hydroxy-*m*-tolyl methyl ether, dissolved in ice-cold aqueous alcohol, is oxidised by ferric chloride to 5:5'-*dimethoxy*-3:3'-*dimethyl*-4:4'-*diphenoquinone* (annexed formula), dark violet needles, m. p. 202—203°, which is reduced by zinc dust and acetic acid to 4:4'-*dihydroxy*-5:5'-*dimethoxy*-3:3'-*dimethyldiphenyl*, colourless crystals, m. p. 188·5—189·5°, which are reconverted into the quinone by ferric chloride. The quinol is demethylated by hydrobromic acid (D 1·48) at 150°, thereby giving 4:5:4':5'-*tetrahydroxy*-3:3'-*dimethyldiphenyl*, m. p. 230—231° (decomp.) after darkening from 220° (*tetra-acetate*, needles, m. p. 193·5—194·5°). 4:4':5:5'-*Tetramethoxy*-3:3'-*dimethyldiphenyl* forms leaflets, m. p. 102—103°.



2:3-Dihydroxytoluene is oxidised by ferric chloride in aqueous solution to the *substance* (annexed formula), bluish-black precipitate; a suitable method of purifying the compound could not be discovered, and its constitution is deduced in part from its analysis, in part from its reduction to a colourless material, which is converted by acetic anhydride into 4:5:4':5'-tetra-acetoxy-3:3'-dimethyldiphenyl. Under similar conditions, hydrourushiol is transformed by ferric chloride into a *substance*, $(C_{42}H_{67}O_4)_2Fe$, bluish-black precipitate, whilst hydrourushiol monomethyl ether gives a reddish-brown, crystalline *precipitate*, $C_{15}H_{31}\cdot C_6H_2O(OMe):C_6H_2O(OMe)\cdot C_{15}H_{31}$, m. p. 120—122°, which is reduced by zinc dust and acetic acid to the colourless *phenol*,

$$C_{15}H_{31}\cdot C_6H_2(OMe)(OH)\cdot C_6H_2(OH)(OMe)\cdot C_{15}H_{31},$$

m. p. 80—81·5°.



An alcoholic solution of 2-hydroxy-*m*-tolyl methyl ether is oxidised by air in the presence of laccase to 5:5'-dimethoxy-3:3'-dimethyl-4:4'-diphenoquinone; an aqueous solution of 2:3-dihydroxytoluene is only slightly affected by air, but, in the presence of laccase, a brown precipitate forms slowly which does not melt below 280°. H. W.

Phenyl-*o*-tolyltellurium Compounds. KARL LEDERER (*Ber.* 1920, **53**, [*B*], 1674—1680. Compare this vol., i, 482, and earlier abstracts).—The action of Grignard's reagents on diaryltelluronium dihaloids leads to the formation of triaryltelluronium salts, which are reduced by an excess of the reagent to tellurides. The latter reaction can occur in three directions, giving (i) a simple telluride $TeR_2R'\cdot Hal. + R'\cdot MgHal. = TeR_2 + R'_2 + MgHal_2$ (this type of

change is frequently observed with magnesium methyl iodide); (ii) a mixed telluride, $TeR_2R'\cdot Hal. + R'\cdot MgHal. = R\cdot TeR' + R\cdot R' + MgHal._2$; or (iii) a mixture of the two possible products. The last type is now exemplified in the action of magnesium phenyl bromide on di-*o*-tolyltelluronium dibromide, or of *o*-tolylmagnesium bromide on diphenyltelluronium dibromide, which leads to the formation of a mixture of simple and mixed tellurides, and thus forms a contrast with the action of magnesium phenyl bromide on di-*p*-tolyltelluronium dibromide, which leads solely to the production of phenyl *p*-tolyl telluride. The mixture of tellurides is converted into the corresponding dibromides, which are separated by fractional crystallisation, and the individual dibromides are subsequently reduced to the corresponding tellurides by magnesium methyl iodide.

Phenyl o-tolyl telluride, $TePh\cdot C_6H_4Me$, is a pale orange-yellow oil, b. p. 212—213°/22 mm. It yields the following derivatives: *dibromide*, microscopic, six-sided platelets or monoclinic rods, m. p. 154—155° after softening at 150—151°; *dichloride*, four-sided rods and hexagonal platelets, m. p. 179—180° after softening at 176°; *di-iodide*, red, monoclinic crystals, m. p. 172—173° after sintering at about 169°; *oxide*, colourless prisms, which soften at 214° and have m. p. 216—217° to a turbid liquid, which becomes transparent at 218°; *mercuri-iodide*, $TePh\cdot C_6H_4Me,HgI_2$, small, yellow needles, m. p. 133—134° after softening at about 123°. *Phenyl-o-tolylmethyltelluronium iodide*, needles, m. p. 119—120° (decomp.) after softening at 116—117°, is generally a stable substance, which appears suitable for the preparation of optically active tellurium compounds. H. W.

The Stability of Solutions of Benzyl Alcohol. DAVID I. MACHT and ALFRED T. SHOHL (*J. Pharm. expt. Ther.*, 1920, **16**, 61—69).—Solutions of benzyl alcohol kept in non-soluble glass vessels preserve their anæsthetic properties completely for long periods of time, and such solutions tend to increase their hydrogen-ion concentration very slowly.

When kept in soft glass containers, the fluid tends to become alkaline, and the drug rapidly deteriorates in anæsthetic efficiency. J. C. D.

Preparation of Benzyl Esters and other Benzyl Derivatives from Benzyl Chloride. M. GOMBERG and C. C. BUCHLER (*J. Amer. Chem. Soc.*, 1920, **42**, 2059—2072).—Benzyl chloride, when heated with the dry salts of various organic acids in the presence of copper as a catalyst, gives fair yields of the corresponding esters. Much higher yields of purer esters are obtained by simply heating benzyl chloride and aqueous solutions of the salts, the mixture being thoroughly stirred all the time. Similarly with aqueous solutions of sodium phenoxides, benzyl chloride gives fair yields of mixtures of benzyl ethers and benzylphenols, the relative proportions of the two products varying with the phenol

used. Good yields of the mixed mono-, di-, and tri-benzylamines were obtained from benzyl chloride and aqueous solutions of ammonium carbonate. The relative proportions of primary, secondary, and tertiary amines varied according to the proportions of the reacting substances. Equally good results were obtained when the ammonium carbonate was replaced by aniline, methylaniline, or *m*- or *p*-toluidine. For the preparation of benzyl cyanide from the chloride and sodium cyanide, it is quite satisfactory to use water as the solvent.

In the preparation of benzyl alcohol by hydrolysis of the chloride, it is preferable to use sodium hydroxide rather than the carbonate, and to keep the time of boiling as short as possible.

W. G.

Interaction between Ester and Alcohol Groups in the Presence of Catalysts. EMIL FISCHER [with ERNST PFÄHLER and FRITZ BRAUNS] (*Ber.*, 1920, **53**, [*B*], 1634—1644).—Glycerol *a-benzoate is moderately rapidly converted in ethereal solution in* the presence of potassium carbonate into a mixture of glycerol and dibenzoin. The process is more conveniently followed with the benzoyl derivatives of ethylene glycol in chloroform solution, whereby it is shown that the change is balanced and attains an equilibrium in the presence of the glycol and the mono- and di-benzoates. Similar phenomena are observed with the esters of monobasic acids. The action of the potassium carbonate appears to be definitely catalytic, since very small amounts of it are sufficient to accelerate the change. The phenomena are strikingly similar to those observed by Purdie (T., 1887, **53**, 391), who found that an exchange of alkyl radicles readily took place between simple esters and alcohols in the presence of a small amount of sodium alkyloxide. It is considered possible that similar displacements may occur among the esters of polyhydroxy-alcohols in the absence of catalysts and at the ordinary temperature, and that herein may be the explanation of the gradual change in melting point observed by Grün to take place when diacyl derivatives of glycerol are preserved, and also of the so-called "ageing" of the natural fats.

The monobenzoate of ethylene glycol, when preserved during twenty-four hours in boiling chloroform solution in contact with anhydrous potassium carbonate, yields a considerable proportion of ethylene dibenzoate, whilst a mixture of molar quantities of the latter and ethylene glycol under similar conditions yields unchanged materials and the monobenzoate. Similarly, ethylene dibenzoate and ethyl alcohol yield ethyl benzoate and the mono- and dibenzoates of ethylene glycol, whilst ethylene glycol and methyl benzoate give unchanged ester and the mono- and di-benzoates of ethylene glycol. Resorcinol monobenzoate becomes decomposed into the dibenzoate and resorcinol, and, conversely, can be obtained from these substances. Glycerol monoacetate is largely transformed into diacetin. Glycerol and methyl benzoate, when heated with sodium methoxide in pyridine–methyl-alcoholic solution, yield glycerol

nzoates. Similarly, glycerol and methyl salicylate give glycerol licylates. *iso*Propylideneglycerol and methyl benzoate under nilar conditions are partly converted into *iso*propylideneglycerol nzoate, whilst tribenzoin and glycerol give a mixture of glycerol ono- and di-benzoates. Methyl benzoate and benzyl acetate are rtly transformed into methyl acetate and benzyl benzoate in loroform solution in the presence of sodium methoxide, or in ethyl-alcoholic sodium methoxide solution.

The following substances have been incidentally prepared during e course of the investigation: *trimethylene glycol monobenzoate*, lourless, relatively mobile oil, b. p. 163—164°/12 mm., D_4^{15} 1·141, d dibenzoate, m. p. 59°, from trimethylene glycol and benzoyl loride in the presence of quinoline; *trimethylene glycol di*-p-*trobenzoate*, long, shining needles, m. p. 120° (corr.) after slight evious softening; *trimethylene glycol mono*-p-*nitrobenzoate*, long edles arranged in clusters, m. p. 49°. H. W.

Melting Point of Acetylsalicylic [o-Acetoxybenzoic] Acid. CAPPELLI (*Giorn. Chim. Ind. Appl.*, 1920, **2**, 291—300).—The elting point of aspirin, determined in a capillary tube, is 132° incipient fusion is taken, or 135° for complete transparency. ee also Dahm, A., 1919, i, 124.] T. H. P.

Isomerism of Formylphenylacetic Esters. V. Anilides d Piperidides of Formylphenylacetic Acid. WILHELM ISLICENUS and RUDOLF ERBE (*Annalen*, 1920, **421**, 119—158). In continuation of previous work (compare A., 1917, i, 268), the ilides and piperidides of formylphenylacetic acid have now been vestigated. In each case, two forms have been isolated, which, cording to the evidence of the ferric chloride reaction and the yer bromine titration method, are to be regarded as enols, and nce also as geometrical isomerides, although it has not yet been und possible to assign a definite structure to each form. The inite enolic behaviour exhibited by each pair of isomerides pears to render the position of the corresponding esters the more markable, and, in this connexion, the authors are not prepared admit the validity of the arguments advanced by Dieckmann ., 1918, i, 15). The additive capacity, which has already been erved to some extent with the methyl and ethyl esters (*loc. cit.*), more marked with the anilides and piperidides, which give stable mpounds with methyl and ethyl alcohols, and, in the latter tance, with water also.

Formic ester is slowly added to an ice-cold solution and pension of phenylacetanilide in dry ether in the presence of ium wire, when the sodium derivative gradually separates. e instability of the latter towards water prohibits the use of the ective acidification method of obtaining the α- or β-anilides, and product is therefore treated with water and immediately run o an excess of dilute ice-cold sulphuric acid, the crude product sisting mainly of the β-anilide. *α-Formylphenylacetanilide*,

OH·CH:CPh·CO·NHPh, colourless, six-sided plates, is prepared in the pure condition by recrystallisation of the crude product from benzene (whereby it is necessary to work rapidly) or, less advantageously, from boiling light petroleum. It has m. p. 68° and, when further heated, resolidifies, and again melts at 98°. In alcoholic solution it gives an immediate dark violet coloration with ferric chloride. It is slowly transformed at the ordinary temperature into the β-modification (more rapidly when heated or when preserved in contact with less benzene than is requisite for complete solution (the dissolved portion, however, consists exclusively of the α-variety). *β-Formylphenylacetanilide* is isolated as described above or by crystallisation of the crude product from ether or glacial acetic acid. It forms colourless, three-sided leaflets m. p. 98° (occasionally higher), is stable in absence of air, but is slowly oxidised by the latter to a viscous, yellow syrup, and, in alcoholic solution, gives an immediate, intense violet coloration with ferric chloride. Either variety gives an additive *compound* with ethyl alcohol, slender needles, m. p. 104—106° (decomp.) which slowly loses alcohol when preserved; the relative stability of the substance, its inability to develop an immediate coloration with ferric chloride, and its failure to decolorise bromine cause it to be regarded as a definite chemical compound,

OH·CH(OEt)·CHPh·CO·NHPh.

The corresponding *product* from methyl alcohol, silky needles m. p. 107—108° (gas evolution), is considerably more stable, and can be preserved unchanged if air is excluded; on exposure to air it slowly eliminates formic acid. When titrated with bromine in alcoholic solution, the α- and β-forms indicate the presence of 96·5% and 98·8% of enol respectively.

The following metallic derivatives of formylphenylacetanilide are described: *sodium* compound, yellowish-white, somewhat unstable, crystalline precipitate, which could not be completely purified; *copper* compound, dark green, microscopic, silky needles m. p. 172—173° (from alcohol), or prisms ($+C_6H_6$) from benzene *iron* compound, slender, red needles, m. p. 207—209°.

Formylphenylacetanilide is converted at 120—140° into β-anilino-α-phenylacrylanilide, NHPh·CH:CPh·CO·NHPh, yellow hexagonal plates or almost colourless needles, m. p. 106—107°, and diphenylcarbamide and phenylacetaldehyde; the former substance is much more smoothly produced by the action of an excess of aniline on formylphenylacetanilide at 60°. With phenylhydrazine the anilide gives the corresponding *phenylhydrazone*, slender colourless needles, m. p. 170—171°, which, at 200—220°, loses aniline and forms 1:4-diphenylpyrazolone, needles, m. p. 194—195°. In one instance, an *additive* compound, small, colourless needles, m. p. 158—160°, was isolated from formylphenylacetanilide and phenylcarbimide, but, in general, for some unexplained reason, the action of the substances results in the evolution of carbon dioxide and production of β-anilino-α-phenylacrylanilide m. p. 106—108°. Saturated alcoholic hydrogen chloride, or, pre-

ferably, concentrated sulphuric acid, converts α- or β-formylphenylacetanilide into β-phenyl-α-carbostyril, colourless needles, m. p. 227—228°. Either form of the anilide (or the corresponding alcoholates) suffers autoxidation on exposure to air, yielding formic acid and benzoylformanilide, m. p. 63—64°, the latter being, however, more smoothly obtained from the anilides by oxidation with potassium permanganate in acetone solution.

Piperidine phenylacetate, long, slender needles, m. p. 101—103°, is converted at 180—200° into *phenylacetopiperidide*, colourless needles, m. p. 5—7°, b. p. 200—203°/12 mm. (which is conveniently purified through the *hydrochloride*, needles, m. p. 84—86°). The piperidide condenses with ethyl formate in ethereal solution in the presence of metallic sodium, yielding *sodium formylphenylacetopiperidide*, colourless, crystalline powder, which could not be completely purified; when suddenly acidified by an excess of cold dilute sulphuric acid, the sodium derivative yields formylphenylacetopiperidide, m. p. 110—116°, which is probably to be regarded as the crude β-form. After being crystallised from a mixture of benzene and light petroleum, it gives *α-formylphenylacetopiperidide*, $HO·CH:CPh·CO·C_5NH_{10}$, indistinct, colourless, microscopic crystals, m. p. 104—106°, which becomes oxidised, with evolution of formic acid, on exposure to air, and yields an immediate violet coloration with ferric chloride. In contrast to the crude product, the pure α-form is soluble in cold water, and the solution gradually deposits crystals of the *hydrate*,

$$CH(OH)_2·CHPh·CO·C_5NH_{10},$$

m. p. 114° (the same substance is obtained when carbon dioxide is passed into an aqueous solution of sodium formylphenylacetopiperidide); the substance is remarkably stable, and does not give an immediate coloration with ferric chloride. When heated in a vacuum at 70—80°, it loses the theoretical quantity of water, leaving a residue, m. p. 122°, which gives a violet coloration with ferric chloride (? β-formylphenylacetopiperidide), but, after repeated crystallisation from benzene and light petroleum, has m. p. 104—106° (α-form). The hydrate is transformed by boiling methyl alcohol into the corresponding *methyl alcoholate*, colourless plates, m. p. 116—117°, and by ethyl alcohol into the *ethyl alcoholate*, microscopic platelets or long prisms, m. p. 98°. *Formylphenylacetopiperididephenylhydrazone* crystallises in colourless, rectangular plates, m. p. 158—159°, which gradually decompose when preserved, and is transformed at 180—200° into piperidine and 1:4-diphenylpyrazolone, m. p. 195—196°.

Phenylacetodiphenylamide, $CH_2Ph·CO·NPh_2$, m. p. 73—74° (Hausknecht gives 72°), is conveniently prepared from phenylacetyl chloride and diphenylamine in the presence of pyridine; when treated with ethyl formate and potassium ethoxide in alcoholic-ethereal solution, it is quantitatively converted into diphenylamine and ethyl formylphenylacetate. A similar result was obtained when metallic sodium and ether were employed, the reaction in this instance occurring very slowly. H. W.

Addition of Aliphatic Aldehydes to Unsaturated Compounds. New Synthesis of δ-Lactones. HANS MEERWEIN (*Ber.*, 1920, **53**, [*B*], 1829—1835).—In continuation of previous work (A., 1919, i, 21), it is shown that aliphatic aldehydes which contain at least one hydrogen atom attached to the carbon atom vicinal to the aldehyde group are pre-eminently capable of condensing with unsaturated aldehydes and ketones, with the formation of dialdehydes or ketonic aldehydes. The additive capacity probably depends on the desmotropic character of the aldehydes; attempts to isolate sodium derivatives by the action of sodium, sodium alkyloxide, or sodamide on ethereal solutions of the aldehydes were not, however, successful, since the corresponding aldols were immediately produced, even at $-40°$. In connexion with the latter observation, it is somewhat surprising that potassium methoxide can be used as condensing agent with aldehydes, but the explanation is found in the fact that aldol formation occurs much more slowly in alcoholic solution than in any other solvent, owing to the reversible production of hemiacetals, OH·CHR·OR′.

The αε-dialdehydes and αε-ketoaldehydes are smoothly converted into the isomeric δ-lactones by an intramolecular Cannizzaro reaction under the influence of alcoholic alkyloxide. The isolation of the dialdehydes or ketoaldehydes in the pure condition is quite unnecessary for this purpose, since by suitable modification of temperature, period of heating, and concentration of alkali it is possible to obtain either the primary product, the δ-lactone, or the corresponding hydroxy-acid.

The additive capacity of aliphatic aldehydes also extends to αβ-unsaturated esters; thus, *iso*butaldehyde combines with methyl benzylidenemalonate to give the *compound*,

$$CHO\cdot CMe_2\cdot CHPh\cdot CH(CO_2Me)_2,$$

m. p. 150—152°, and this points the way to a possible simple synthesis of δ-aldehydo-acids.

Finally, αβ-unsaturated aldehydes, which contain at least one hydrogen atom attached to the carbon atom vicinal to the double bond, readily condense with other unsaturated substances; thus, α-methyl-β-ethylacraldehyde unites with phenyl styryl ketone, yielding the *compound*, $CH_2Bz\cdot CHPh\cdot CHMe\cdot CH{:}CMe\cdot CHO$. The last reaction explains the transformations suffered by acetophenone when heated with sodium ethoxide; in all cases, the primary product is dypnone, COPh·CH:CMePh, which, as an αβ-unsaturated ketone, readily unites with other unsaturated compounds, thus yielding dypnopinacone, $CHBz{:}CPh\cdot CH_2\cdot CMePh\cdot CH_2Bz$, and the compound, $\begin{array}{l} CPh\text{—}CH{:}CPh \\ \| \qquad\qquad\quad | \\ CBz\cdot CMe{:}CH \end{array}$, described by Castaldi (this vol., i, 391).

[With GEORG KILLING.]—*γ-Benzoyl-β-phenyl-αα-dimethyl*-n-*butaldehyde*, $CH_2Bz\cdot CHPh\cdot CMe_2\cdot CHO$, needles, m. p. 105—106°, which decomposes when further heated into its components, is prepared by warming a methyl-alcoholic solution of phenyl styryl ketone and *iso*butaldehyde with a solution of potassium methoxide at 40°; the aldehyde is oxidised by chromic acid to γ-benzoyl-β-

phenyl-*αα*-dimethyl-*n*-butyric acid, m. p. 160°. If the reaction mixture is allowed to remain in contact with a further quantity of potassium methoxide, the corresponding lactone is obtained, which, however, is somewhat difficult to isolate, so that it is preferable to convert it first into *δ-hydroxy-βδ-diphenyl-αα-dimethyl-n-valeric acid*, $OH\cdot CHPh\cdot CH_2\cdot CHPh\cdot CMe_2\cdot CO_2H$, rhombic prisms, m. p. 154—155°, from dilute acetic acid, prismatic plates ($+CHCl_3$) from chloroform, which yields the *lactone*, coarse needles, m. p. 106—107°, when heated at 200°.

[With KARL STEINACKER.]—*αγγ-Trimethyl-β-ethyl-δ-valerolactone*,

$$\begin{array}{l} CHEt\cdot CHMe\cdot CO \\ | \qquad\qquad\qquad\quad | \\ CMe_2—CH_2—O \end{array}$$

almost colourless, mobile oil, b. p. 140°/17—18 mm., D_4^{20} 0·9892, n_D^{20} 1·46412, is obtained from *iso*butaldehyde and *α*-methyl-*β*-ethylacraldehyde; the corresponding hydroxy-acid is unstable in the free state, and is oxidised by potassium permanganate to *ααγ-trimethyl-β-ethylglutaric acid*, $CO_2H\cdot CMe_2\cdot CHEt\cdot CHMe\cdot CO_2H$, small, prismatic crystals, m. p. 135—136°. H. W.

Reactions with α-Campholide and Ethyl Bromocampholate. H. RUPE and A. JÄGGI (*Helv. Chim. Acta*, 1920, **3**, 654—668).—*α*-Campholide may be obtained in almost theoretical yield by heating camphoric anhydride in contact with a nickel catalyst and in a current of hydrogen, using an electric furnace, as previously described (A., 1919, i, 29, 334). When the temperature of the furnace is too high and the current of hydrogen insufficient, the campholide formed is accompanied by volatile oils, consisting partly of oxygenated compounds and partly of unsaturated hydrocarbons of the formula C_9H_{16}.

By a slight modification of Baeyer and Villiger's method of preparation (A., 1900, i, 133), bromocampholic acid may be obtained in 80% yield; the acid crystallises in plates or leaflets, m. p. 177° (decomp.). The following derivatives of the acid have been prepared. The *chloride*, $C_{10}H_{16}OClBr$, best obtained with the help of thionyl chloride, forms stout crystals of monoclinic habit, m. p. 57·5°; the *amide*, $C_{10}H_{18}ONBr$, fine needles, m. p. 207°; the *anilide*, $CH_2Br\cdot C_8H_{14}\cdot CO\cdot NHPh$, white needles, m. p. 142°; the *phenylhydrazide*, $CH_2Br\cdot C_8H_{14}\cdot CO\cdot NH\cdot NHPh$, slender needles, m. p. 150—151°; the *methyl* ester, colourless, greasy oil, b. p. 139°/15 mm.; the *ethyl* ester, m. p. 9—10°, b. p. 142—143°/13 mm.; the *phenyl* ester, colourless plates, m. p. 46—47°, b. p. 204°/11 mm.

A compound, $C_{24}H_{30}O$, which may be *3-phenylethyl-1:2:2-trimethyl*cyclo*pentane 1-benzyl ketone* (?),

$$CH_2Ph\cdot CH_2\cdot C_8H_{14}\cdot CO\cdot CH_2Ph,$$

obtained in small yield by the interaction of ethyl bromocampholate and magnesium benzyl chloride, forms large, shining leaflets, m. p. 119°, b. p. 245—250°/14 mm.

When heated with quinoline, aniline, or dimethylaniline, ethyl bromocampholate loses ethyl bromide, giving *α*-campholide. When heated with methyl-alcoholic potassium hydroxide, however, it loses

only hydrogen bromide, yielding *ethyl* 1 : 2 : 2-*trimethyl*-3-*methylene*cyclo*pentane*-1-*carboxylate*, $CH_2{:}C_8H_{13}{\cdot}CO_2Et$, which is a colourless oil of pleasant, aromatic odour, b. p. 93°/12 mm., $[\alpha]_C^{20}+20{\cdot}62°$ (12·99°), $[\alpha]_D^{20}+26{\cdot}73°$ (16·38°), $[\alpha]_{Hg\,(546{\cdot}3\,\mu\mu)}^{20}+31{\cdot}57°$ (18·97°), $[\alpha]_F^{20}$ 41·24° (25·41°) (the values in brackets being for its solution in benzene), n_α 1·45575, n_D 1·45773, n_β 1·46446, n_γ 1·47005; when treated with bromine in chloroform, this unsaturated ester yields its *bromo*-derivative, $C_{12}H_{19}O_2Br$, m. p. 149°.

1 : 2 : 2-*Trimethyl*cyclo*pentane*-1 : 3-*dimethanol*,

$$\begin{matrix} CH_2\text{—}CH(CH_2{\cdot}OH) \\ | \\ CH_2{\cdot}CMe(CH_2{\cdot}OH) \end{matrix}\!\!>\!CMe_2,$$

obtained by reducing α-campholide with sodium and alcohol, forms long, shining needles, m. p. 130°, b. p. 151—154°/12 mm.

α-Camphidone (compare Oddo and Leonardi, A., 1897, i, 86; Tafel and Eckstein, A., 1902, i, 43; Rupe and Splittgerber, A., 1907, i, 1016; Tafel and Bublitz, A., 1906, i, 43) may be prepared in good yield by heating α-campholide in a sealed tube with zinc chloride and ammonia, and camphidine (Tafel and Eckstein, *loc. cit.*) may be obtained by similar treatment of the above glycol.

T. H. P.

The Vapour Pressure of Phthalic Anhydride. K. P. Monroe (*J. Ind. Eng. Chem.*, 1920, **12**, 969—971. Compare this vol., i, 164).—The vapour pressure of phthalic anhydride at various temperatures was found to be as follows:

t	212·0°	222·0°	234·6°	241·5°	252·4°	284·6°
p (mm. Hg)	130·5	172·1	241·2	287·1	369·4	759·3

The interpolation formula applicable to these data is: $\log_{10} p = 7{\cdot}94234 - 2823{\cdot}5/T$, where p is the vapour pressure in mm. of mercury and T the absolute temperature. W. P. S.

A New Class of Hypnotics. The Dialkylhomophthalimides. Auguste Lumière and Félix Perrin (*Compt. rend.*, 1920, **171**, 637—639).—Dialkylhomophthalimides of the type

$$C_6H_4\!\!<\!\!\begin{matrix} CRR'{\cdot}CO \\ \quad\quad | \\ CO\text{——}NH \end{matrix}$$

may readily be obtained by the action of the corresponding alkyl iodides on homophthalimide in the presence of sodium ethoxide. The following have been prepared: *diethylhomophthalimide*, m. p. 144°; *ethylpropylhomophthalimide*, m. p. 117°; *dipropylhomophthalimide*, m. p. 128°; *diallylhomophthalimide*, m. p. 140—141°. All these compounds are hypnotics, whilst, at the same time, their toxicity is very slight, and they are apparently free from any unfavourable secondary action. W. G.

Some Derivatives of Phthalide. J. Herzig [with Hedwig Brunner and Marianne Schleiffer] (*Annalen*, 1920, **421**, 283—292).—In connexion with the work on gallo-flavin (this vol.,

i, 863), it has been found necessary to repeat the *investigations* of Bargellini and Molina (A., 1912, i, 773) on 3:4:5-trimethoxyphthalide. The preparation of 3:4:5-trimethoxytrichloromethylphthalide, $C_6H(OMe)_3<\begin{matrix}CO\\CH(CCl_3)\end{matrix}>O$, by the action of chloral on methyl trimethylgallate, could not be satisfactorily repeated, but by hydrolysis of the crude product of the action, followed by treatment with diazomethane, it was found possible to isolate *methyl 3:4:5-trimethoxyphthalidecarboxylate*,

$$C_6H(OMe)_3<\begin{matrix}CO\\CH(CO_2Me)\end{matrix}>O,$$

monoclinic crystals, $a:b:c=1{\cdot}1366:1:0{\cdot}6983$, $\beta=122°33'$, m. p. 119—121°, in reasonable yield, which is hydrolysed by methylalcoholic potassium hydroxide to 3:4:5-trimethoxycarboxyphthalide, m. p. 146—149° (Bargellini and Molina give m. p. 142—143°). Distillation under diminished pressure or treatment with sodium acetate and acetic anhydride (but not with the latter alone) transforms the acid quantitatively into 3:4:5-trimethoxyphthalide, monoclinic crystals, $a:b:c=0{\cdot}9548:1:0{\cdot}9640$, m. p. 133—135° (Bargellini and Molina, m. p. 134—135°).

The melting point of 3:4:5-trimethoxy-*o*-phthalic acid has been recorded as 175—176° by Windaus (A., 1911, i, 904), 174° by Bargellini and Molina (*loc. cit.*), and still higher by Feist (A., 1908, i, 100); a specimen prepared by the oxidation of 3:4:5-trimethoxyphthalide had the constant m. p. 145—148° (decomp.), and readily yielded the corresponding *methyl* ester, m. p. 62—65°. A specimen prepared by the authors, and subsequently recrystallised three times from a mixture of ether and light petroleum by Windaus, had m. p. 171° after some previous softening. Apparently, the conversion of the acid into the anhydride is greatly catalysed by traces of impurity, possibly derived from the alkali of the glass capillaries.

Methyl 2:3-dimethoxybenzoate condenses with chloral hydrate in the presence of concentrated sulphuric acid, with the formation of *5:6-dimethoxytrichloromethylphthalide*, m. p. 105—107° (Fritsch, A., 1898, i, 663, gives 104°), which is hydrolysed with some difficulty to *5:6-dimethoxycarboxyphthalide*,

$$C_6H_2(OMe)_2<\begin{matrix}CO\\CH(CO_2H)\end{matrix}>O,$$

m. p. 151—154°. The latter is quantitatively transformed into 5:6-dimethoxyphthalide, m. p. 99—101°, when distilled under diminished pressure. No evidence of the formation of Fritsch's 2-carboxy-3:4-dimethoxymandelic acid could be observed.

H. W.

The Bile Acids. VI. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1919, **107**, 152—156).—Cilianic acid and hydroxylamine hydrochloride were dissolved in 10% sodium hydroxide, and, after heating in steam for a few hours, the mixture was left for twenty-

four to forty-eight hours at the ordinary temperature. On th addition of dilute hydrochloric acid, a pasty precipitate wa formed. The precipitate, as well as the filtrate, was extracte with ether, and the ethereal extract evaporated at the ordinar temperature, and eventually in a vacuum. A white, amorphou substance was thus obtained, which gave Lassaigne's reaction This substance was extracted twice with ether (fractions *A* and *B*) leaving a residue fraction, *C*. The three fractions commence liquefying at about 100° and frothing about 120—125°, afte which temperature they decomposed. The nitrogen analyses of al three fractions agreed with the figures for the *oxime* of ciliani acid, $C_{24}H_{34}O_9$:NOH, in which only one ketone group react with the hydroxylamine. The theory of the formation of ciliani acid from bilianic acid, and its bearing on the other inactive keton group, is discussed. S. S. Z.

Unsaturated Bile Acids. FR. BOEDECKER (*Ber.*, 1920, **53**, [*B* 1852—1862).—The only unsaturated bile acids which have bee isolated previously are cholatrienecarboxylic acid (Wieland an Weil, A., 1912, i, 830) and choladienecarboxylic acid (Wieland an Sorge, A., 1917, i, 685), which are obtained from cholic and deoxy cholic acids, respectively, by distillation under diminished pressure and in which the hydroxyl groups of the parent acids are com pletely absent. The author has examined the behaviour of choli acid towards milder dehydrating agents (molten glycollic acid an potassium hydrogen sulphate, dilute sulphuric acid, zinc chlorid oxalic acid, phosphoric acid), and has obtained products fro which an unsaturated dihydroxy-bile acid, $C_{24}H_{38}O_4$, can b isolated in good yield, and for which he proposes the nam *apo*cholic acid. It follows that one of the three secondar hydroxy-groups of cholic acid is particularly readily eliminate under the action of dehydrating agents, whilst the remaining tw are considerably more firmly retained. Now Borsche (A., 191 i, 276) has shown that two hydroxyl groups are present in th same positions in the molecules of cholic and deoxycholic aci and, if the third hydroxyl group of the former is the one whic is lost, *apo*cholic acid must be an unsaturated derivative of deox cholic acid. The direct hydrogenation of *apo*cholic to deoxychol acid has not been effected up to the present, since the substance peculiarly resistant to the action of hydrogen, but the two aci are so similar in their general chemical behaviour that they ca readily be mistaken the one for the other.

Cholic acid is converted by zinc chloride in boiling acetic aci solution into a mixture of unchanged material, apo*cholic ac* and less saturated acids; the latter are separated by treatme with cold ether, and are recovered from the ethereal solution as pale yellow resin. Cholic and *apo*cholic acids are separated b taking advantage of the sparing solubility of the former in co alcohol, in which the latter dissolves readily. The crude *apo*chol acid is converted into its compound with acetic acid, and the latt

is crystallised from aqueous alcohol, the product being ultimately heated at 120—130°/0·1—0·3 mm. *apo*Cholic acid has m. p. 173—174°, $[\alpha]_D^{20}$ +49·87° in absolute alcoholic solution; it immediately decolorises alkaline potassium permanganate solution, readily absorbs bromine, with the formation of a *dibromide*, and gives a coloration with acetic anhydride and sulphuric acid similar to, but more decided than, that of deoxycholic acid. Its *alkali* salts are freely soluble in water, but the *calcium*, *barium*, and *strontium* salts are precipitated as plaster-like masses. The *magnesium* salt crystallises in very characteristic, slender needles; the *silver* salt was analysed. The following additive compounds are described: *acetic-apocholic acid*, $C_{24}H_{38}O_4,C_2H_4O_2$, small, colourless prisms, m. p. 135—155° after previous softening according to the manner of heating, $[\alpha]_D^{20}$ +45·35° in alcoholic solution, which obstinately retains a portion of the acetic acid, even after protracted heating; *butyric-apocholic acid*, $(C_{24}H_{38}O_4)_2,C_4H_8O_2$, needles, m. p. about 170°; *palmitic-apocholic acid*, $(C_{24}H_{38}O_4)_8,C_{16}H_{32}O_2$, slender needles, m. p. 184—185°, $[\alpha]_D^{20}$ +43·7° in absolute alcohol; *stearic-apocholic acid*, needles, m. p. 185—186°; a compound could not be obtained with formic acid; with *benzene*, needles, m. p. 174—175°; with *xylene*, $(C_{24}H_{38}O_4)_2,C_8H_{10}$, hexagonal plates, m. p. 171—172° after previous softening; with *naphthalene*,

$$(C_{24}H_{38}O_4)_2,C_{10}H_8,$$

slender needles, m. p. 173—174°, $[\alpha]_D^{20}$ +41·20° in absolute alcohol; with *ethyl alcohol*, slender needles, which lose alcohol on exposure to air; with *ethyl acetate* or *acetone*, unstable prisms; with *benzaldehyde*, needles, m. p. 156°; with *d-camphor*, $C_{24}H_{38}O_4,C_{10}H_{16}O$, small needles, m. p. 179—180° after softening at 177°, $[\alpha]_D^{20}$ +43·80° in ethyl-alcoholic solution.

Methyl apocholate has m. p. 88—90° after slight previous softening; it retains a part of the ability of the parent acid to form additive compounds, and thus yields the *substances*,

$$C_{24}H_{37}O_4Me,MeOH,$$

long prisms, m. p. 83—84° after softening at 75°, which slowly loses methyl alcohol on exposure to air, and $C_{24}H_{37}O_4Me,C_2H_4O_2$, large prisms, m. p. 87—88° after slight softening at 85°.

H. W.

The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. I. Some Derivatives of *cyclo*Pentene and *dicyclo*Pentane. ERNEST HAROLD FARMER and CHRISTOPHER KELK INGOLD (T., 1920, **117**, 1362—1373).

The Resolution of the Keto-dilactone of Benzophenone-2 : 4 : 2′ : 4′-tetracarboxylic Acid. WILLIAM HOBSON MILLS and CHARLES REYNOLDS NODDER (T., 1920, **117**, 1407—1410).

Tannins. VI. Chebulic Acid. II. KARL FREUDENBERG and BRUNO FICK (*Ber.*, 1920, **53**, [*B*], 1728—1736. Compare A., **1919**, i, 412).—Chebulic acid is decomposed by hot water into an amorphous acid and a crystalline tannin, which has been pro-

visionally regarded as a digalloylglucose. This hypothesis is now fully confirmed by observations on its degradation under the influence of tannase (compare this vol., i, 562); the increase in acidity and the relative proportions of gallic acid and dextrose can only be explained if the substance is regarded as a digalloylglucose, and this is confirmed by the results of the elementary analysis of the substance itself and of its crystalline *acetyl* derivative [di(triacetylgalloyl)-triacetylglucose, coarse needles, m. p. 177—179°], and of determinations of molecular weight, which can be effected in boiling acetone. The digalloylglucose is unaffected by emulsin, phaseolunatase, or yeast extract, and thus differs from the 1-galloyl-β-glucose recently described by Fischer and Bergmann (A., 1919, i, 89). It is possibly a derivative of α-glucose, but probably the 1-position of the sugar is free, aud, in chebulinic acid, attached to the amorphous acid. Investigation of the latter is as yet incomplete. It does not crystallise in the free state. In addition to the thallium salt described previously (*loc. cit.*), the *brucine* salt, m. p. about 250° after darkening above 200°, has now been investigated. The composition of both these salts indicates that it is a dibasic acid, $C_{14}H_{14}O_{11}$, but it possibly contains a third, feebly acidic, group, since the equivalent, as determined by titration with litmus as indicator, corresponds with about $\frac{1}{3}C_{14}H_{14}O_{11}$. It yields pyrogallol when distilled under diminished pressure. The suggested formula, $C_{14}H_{14}O_{11}$, can be brought into harmony with the composition of chebulic acid if the latter is regarded as formed from digalloylglucose and the acid with the oss of two molecules of water: $C_{20}H_{20}O_{14} + C_{14}H_{14}O_{11} = C_{34}H_{80}O_{23} + 2H_2O$. Such a new formula for chebulic acid is in agreement with the most trustworthy analytical data recorded in the literature and with the molecular weight as determined by titration and by the ebullioscopic method with acetoue as solvent. It also explains satisfactorily the observations recorded in the previous communication on the fission of chebulic acid.

It is, however, quite possible that the "fission acid" has only half the assumed molecular weight, although the composition of the salts does not harmonise so well for an acid such as $C_7H_6O_6$, and the explanation of the optical activity is difficult; in this case, two such molecules must be present in the molecule of chebulic acid. The hypothesis that the "fission acid" is actually a mixture, possibly of $C_7H_6O_6$ and $C_7H_8O_5$, would explain many of its properties and be reconcilable with other observations, such as the ratio of the amounts of degradation products obtained from chebulic acid. Lastly, it is also possible that a third, readily detached gallic acid residue is present in chebulic acid. H. W.

The Synthesis of β-Keto-bases from Amine Salts, Formaldehyde, and *cyclo*Hexanone. C. MANNICH and R. BRAUN (*Ber.*, 1920, **53**, [*B*], 1874—1880).—The synthesis, previously applied to aliphatic ketones (A., 1917, i, 634), has now been extended to *cyclo*hexanone.

1-*Dimethylaminomethyl*cyclo*hexan-2-one hydrochloride*, colour less crystals, m. p. 152°, is readily obtained in 85% yield by th interaction of *cyclo*hexanone in formaldehyde solution and di methylamine hydrochloride. The corresponding free *base*,

$$\begin{array}{l} H_2C\cdot CH_2\cdot CH\cdot CH_2\cdot NMe_2 \\ H_2C\cdot CH_2\cdot CO \end{array},$$

has b. p. about 100°/13 mm., and cannot be long preserved at th ordinary temperature; the *picrate*, pale yellow needles, m. p 149°, *perchlorate*, m. p. 156°, and *aurichloride*, yellow prisms m. p. 132°, are described. The *methiodide* is very unstable decomposing at the ordinary temperature into trimethylammonium iodide and methylene*cyclo*hexanone. The keto-base yields a *oxime hydrochloride*, very hygroscopic rods, m. p. 158°, and *cyanohydrin*, broad needles, m. p. 55°; it is oxidised to adipi acid by potassium permanganate or nitric acid. Reduction by means of aluminium amalgam and moist ether converts the keton into 1-*dimethylaminomethyl*cyclo*hexan-2-ol*, colourless, stable oil b. p. 108°/13 mm. [the *hydrochloride*, very hygroscopic crystals m. p. 160°, *picrate*, *acetate*, colourless liquid, b. p. 136°/13 mm (*hydrochloride*, m. p. 141°), and *benzoate*, viscous oil (*hydro chloride*, needles, m. p. 220°), are described].

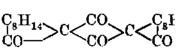
The condensation of methylamine hydrochloride, formaldehyde and *cyclo*hexanone takes a more complicated course, but it ha been found possible to isolate the following substances in the pur condition: (i) 1-methylene*cyclo*hexan-2-one, b. p. 65°/13 mm *semicarbazone*, m. p. 195°; (ii) the *ether*, $O(CH_2\cdot C_6H_9O)_2$, rods m. p. 149°, the constitution of which is deduced from its analysis its inactivity towards acetic anhydride, and the formation of *semicarbazone* and a *bisphenylhydrazone*, m. p. 191°; and (iii *bis*cyclo*hexanonylmethylmethylamine*, $MeN\left[\begin{array}{l} CH_2\cdot CH\cdot CH_2\cdot CH_2 \\ \quad\quad CO-CH_2\cdot CH_2 \end{array}\right]$ needles, m. p. 172° (the hygroscopic *hydrochloride*, *aurichloride platinichloride*, *picrate*, yellow needles, m. p. 175°, and *methiodide* quadratic crystals, m. p. 144°, are described).

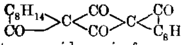
Similarly, ammonium chloride, formaldehyde, and *cyclo*hexan one give *tri*cyclo*hexanonylmethylamine*, $N\left[\begin{array}{l} CH_2\cdot CH_2\cdot CH_2\cdot CH_2 \\ \quad\quad CO-CH_2\cdot CH_2 \end{array}\right]$ slender crystals, m. p. 119°; *hydrochloride*, coarse, colourles crystals, m. p. 110°. H. W.

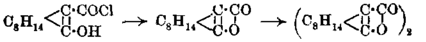
Preparation of β-Tetrahydronaphthyl Methyl Ketone ALBERT R. F. HESSE (*Ber.*, 1920, **53**, [*B*], 1645).—It has bee observed by Scharwin (A., 1902, i, 625) that acetyl chloride react unusually energetically with tetrahydronaphthalene, and tha tetrahydronaphthyl methyl ketone can only be isolated in the pur state from the product by repeated fractional distillation. Th difficulties attendant on the preparation have been ascribed b von Braun to the presence of dihydronaphthalene in the origina material, and this suggestion appears to be confirmed by th

author's observation that pure tetrahydronaphthalene reacts slov with acetyl chloride in carbon disulphide solution in the preser of aluminium chloride, with the production of β-tetrahyd naphthyl methyl ketone, b. p. 182°/20 mm., which is obtained the pure condition after a single distillation, and in almost 9(yield. The ketone is conveniently characterised as its *semica: azone*, m. p. 234—235°. H. W.

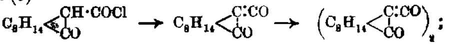
Relationships between the Dimeric Ketens and *cy(* **Butane-1 : 3-dione and its Derivatives.** G. Schroeter (*B(* 1920, **53**, [*B*], 1917—1926).—A reply to Staudinger's critici: (this vol., i, 517) on the author's conception of dimeric ketens "polymolecules," in which the components are not united by ma or subsidiary atomic valencies, but by molecular valencies (*A* 1917, i, 145).

The isolation of two camphorketens, 

and , has been considered by Stauding as strong evidence in favour of regarding such substances as aton compounds, but the author points out that the *cis-trans* natu of the isomerism has been by no means definitely established. T two forms differ most widely in their specific rotations in benze: and ethyl acetate solutions, and such considerable divergence more readily explained by the assumption of structural isomeris: the greater specific rotation of the one isomeride being due to t presence in it of a double bond in close proximity to the asyı metric carbon atom. The argument is illustrated at the instan of methyl camphorcarboxylate, which, in the ketonic form, h $[\alpha]_D$ +18·40° in benzene solution (mean value of a large numb of determinations, in which $c = 0{\cdot}3 - 3{\cdot}0$); in alcohol, ethyl acetat acetone, ether, and chloroform, the values of $[\alpha]_D^{20}$ are +59·58 59·00°, 54·39°, 62·66°, and 62·33°, respectively, and each of the solutions contains an equilibrium mixture. The complete enolised ester has $[\alpha]_D^{20}$ about +154° in benzene or alcohol, althoug this value is a little uncertain by reason of the unascertain(influence of the sodium alkyloxide added as enolising agent. It certain, however, that the specific rotation of the enol is abo: eight times that of the ketone, and similar differences are record(for other keto-enolic desmotropes in the camphor series. appears therefore valid to conclude that Staudinger's campho ketens are keto-enolic isomerides, which may be regarded as form(from the desmotropic forms of camphorcarboxylyl chloride : accordance with the schemes:

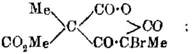
(*a*) 

and (*b*)

;

the form (*a*), which contains an olefinic double bond in close proximity to the two asymmetric carbon atoms, exhibits the higher optical activity.

The *cyclo*butane-1 : 3-diones cannot be considered as 1 : 3-*cyclo*-butenolones, since they behave towards metals in indifferent media precisely as diketones, and are only attacked after addition of an enolising solvent, such as alcohol. Staudinger's explanation of the phenomena as due to passivity of the metal is insufficient, since the enolic forms react as strong acids. The author justifies his previous position with respect to the isomerism of the methyl-ketencarboxylic esters, $(CO_2Me\cdot CMe\!:\!CO)_2$, and methyl 1 : 3-dimethyl*cyclo*butanedionedicarboxylate, $\genfrac{}{}{0pt}{}{Me}{CO_2Me}{>}C{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C{<}\genfrac{}{}{0pt}{}{Me}{CO_2Me}$; and finds in the action of bromine (giving an additive product, which spontaneously eliminates methyl bromide) further evidence in favour of his mode of formulating the latter substance, since the reaction is readily explained by the intermediate formation of the product $\genfrac{}{}{0pt}{}{Me}{CO_2Me}{>}C{<}\genfrac{}{}{0pt}{}{COBr}{-CO-}{\!\!\!-}CBr{<}\genfrac{}{}{0pt}{}{CO_2Me}{Me}$, which subsequently passes into the more stable anhydride,



the reaction is thus precisely analogous to the transformation, recorded by Staudinger, of the methyl ester of camphoryl chloride into a brominated camphoric anhydride under the influence of bromine at a low temperature.

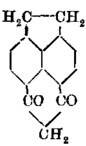
The transformation of dimeric ketens into ketones and derivatives of β-ketocarboxylic acids cannot be regarded as evidence of their constitution, since they are readily depolymerised to the highly reactive simple ketens, which can readily unite with carboxylic acids or their derivatives to β-keto-acids. Further, the reverse transition of a true *cyclo*butane-1 : 3-dione into a dimeric keten has not, so far, been observed, and so long as this is the case the substances cannot be regarded as keto-enolic desmotropes.

H. W.

Malonyl Bromide and a Synthesis of *peri*Acenaphth-indandione. KARL FLEISCHER, HEINRICH HITTEL, and PAUL WOLFF (*Ber.*, 1920, **53**, [*B*], 1847—1852).—The synthesis of a large number of indandiones has been described by Fleischer and his co-workers, but these substances have almost invariably been prepared by the aid of dialkylmalonyl chlorides; attempts to prepare unsubstituted compounds have generally been unsuccessful by reason of the instability of malonyl chloride. Since, however, Fleischer and Wolff (this vol., i, 541) have found that oxalyl bromide is more suitable than oxalyl chloride for ring formation, on account of the greater mobility of the halogen atoms, the authors have turned their attention to the possibilities of malonyl

bromide, and find that this substance also gives considerably better results than the corresponding chloride.

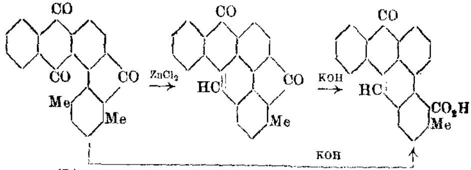
Malonyl bromide, pale yellow, heavy liquid with a distinct green fluorescence, which fumes strongly on contact with the atmosphere, and gradually becomes brown when preserved, b. p. 55—57°/11 mm., is prepared by passing an excess of dry hydrogen bromide into ice-cold malonyl chloride. It reacts with acenaphthene dissolved in carbon disulphide in the presence of aluminium chloride to yield peri*acenaphthindandione* (annexed formula), yellowish-brown, rectangular rods or small needles united in clusters, which become discoloured, but do not melt, below 300° (a similar experiment with malonyl chloride did not yield this substance). The constitution of the compound is deduced from its oxidation by fuming nitric acid to a mixture of mellophanic acid, $C_{10}H_6O_8$, m. p. 239—241°, and naphthalene-1 : 4 : 5 : 8-tetracarboxylic acid, colourless needles, not melting below 300°, which has been obtained previously by Freund and Fleischer (A., 1913, i, 1075) by oxidation of 5-*iso*butyrylacenaphthen-6-carboxylic acid.



H. W.

Synthesis of a Phenanthra-anthraquinonefluorenone. ALFRED SCHAARSCHMIDT and JOHANN HERZENBERG (*Ber.*, 1920, **53**, [*B*], 1807—1814. Compare A., 1919, i, 26).—Chloroanthraquinone-2-carboxylic acid is converted by phosphorus pentachloride into the acid chloride, which condenses with *p*-xylene in the presence of aluminium chloride to yield 1-*chloro*-2-p-*xyloylanthraquinone*, $C_{14}H_6O_2Cl\cdot CO\cdot C_6H_3Me_2$, pale yellow, shining needles, m. p. 175—176°, the success of the preparation being greatly dependent on the purity of the xylene. 1-*Amino*-2-p-*xyloylanthraquinone*, compact, reddish-brown needles or leaflets, m. p. 146—147°, prepared by heating the preceding substance with alcoholic ammonia at 180—190°, is diazotised in concentrated sulphuric acid solution, and the product is treated with copper powder, whereby *dimethyl*-1 : 2-*anthraquinonefluorenone* [3 : 4-*phthalyl*-5 : 8-*dimethylfluorenone*] (formula I), yellowish-brown leaflets with an intensely green fluorescence, m. p. 256°, is obtained, together with 1-*methylphenanthra-anthraquinonefluorenone* (formula II), pale brown, amorphous powder, which volatilises without melting at 370—400°, the substances being separable by crystallisation from pyridine or carbon disulphide; minor amounts of 1-*hydroxy*-2-p-*xyloylanthraquinone* (which was not further investigated) and 2-p-*xyloylanthraquinone*, m. p. 159° (which was also prepared from anthraquinone-2-carboxylyl chloride, *p*-xylene, and aluminium chloride, and yields an intensely green vat with hyposulphite), were also isolated. The constitution of 1-methylphenanthra-anthraquinonefluorenone follows from its formation by dehydrating agents, such as zinc chloride or sulphuric

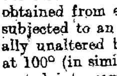
acid, from *p*-dimethylanthraquino-2 : 1-fluorenone. Either substance is converted by fusion with potassium hydroxide into a *methylphenanthra-anthraquinonecarboxylic acid* (formula III), reddish-brown, amorphous substance, which could not be crystallised by reason of its very sparing solubility in all media; the corresponding *silver* salt was analysed.



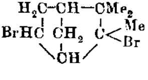
(I.) (II.) (III.)

H. W.

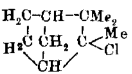
The Camphene Series. I. Mechanism of the Transformation, *iso*Borneol ⇌ Camphene. HANS MEERWEIN and KONRAD VAN EMSTER (*Ber.*, 1920, **53**, [*B*], 1815—1829).—The unusual phenomena attendant on the conversion of *iso*borneol into camphene have usually been explained by the assumption of the intermediate formation of tricyclene; this hypothesis is, however, rendered improbable by the authors' observation of similar changes in the dehydration of monocyclic alcohols, which are structurally similar to *iso*borneol, and it appears more probable that the intermediate product is a compound with a bivalent carbon atom (annexed formula). Attempts were therefore made to form such a substance, and camphorhydrazone was, for this purpose, treated with yellow mercuric oxide, thereby giving the *mercury* compound, $C_8H_{14}<\begin{matrix}CH_2\\ C:N\cdot NH\cdot Hg\cdot OH\end{matrix}$, which, when warmed in alcoholic suspension, was, however, smoothly transformed into tricyclene. The idea of the intermediate formation of a compound with bivalent carbon must therefore be abandoned. Tricyclene, which can readily be obtained from easily accessible materials in this manner, has been subjected to an extended examination, and is found to be practically unaltered by protracted treatment with sulphuric acid (33%) at 100° (in similar circumstances, *iso*borneol is almost entirely converted into camphene), and to react with chloroacetic acid with considerably less readiness than does camphene. It is therefore impossible that tricyclene should be an intermediate product of the transformation of *iso*borneol or its esters into camphene. In



general, it is shown that fission of the trimethylene ring in tr cyclene occurs most readily between the 1:2- or 1:6-carbon atoms thus, it is reduced by hydrogen and nickel at 180—200° t *iso*camphane, b. p. 163°, m. p. 57°, possibly after isomerisation t camphene. Addition of bromine leads t the formation of a liquid *dibromide* (prol ably annexed formula), from which crysta of pinene or camphene dibromide cannot b caused to separate, and which readil loses one atom of bromine when boile

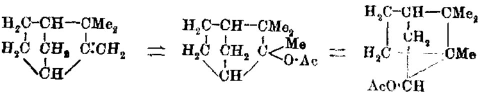


with alcoholic alkali. When gaseous hydrogen chloride is passe into an ethereal solution of tricyclene (or of camphene), crysta line *camphene hydrochloride* (annexed formula), m. p. abo 125—127°, separates in 70% yield; the sul stance is characterised by the unusual mobilit of the chlorine atom and the readiness wit which it eliminates hydrogen chloride. Th latter phenomenon is rapidly exhibited by th freshly prepared substance, and appears to b



catalytically accelerated by acids. The chloride is slowly decon posed by cold water, with production of camphene hydrate, m. p 146—147°, and so rapidly by $N/2$-alcoholic alkali that it can b smoothly titrated with such cold solutions. Its most remarkabl property, however, is its tendency towards transformation int *iso*bornyl chloride, m. p. 158°, which occurs slowly at the ordinar temperature, rapidly in a sealed tube at 130—140°, or by dige tion with methyl-alcoholic or ethereal hydrogen chloride at th ordinary temperature. This behaviour explains why previou attempts to prepare camphene hydrochloride have invariably le to products containing more or less *iso*bornyl chloride. The latte is far more stable towards $N/2$-alcoholic potassium hydroxid solution, but the chlorine atom can be removed quantitatively b boiling the substance with the reagent for half an hour; pinen hydrochloride is practically unaffected by this treatment. simple method is thus given for approximately estimating th proportions of camphene hydrochloride, *iso*bornyl chloride, an pinene hydrochloride in a mixture of the three products. Th camphene hydrochloride–*iso*bornyl chloride transformation ha been examined in this manner, and it is shown that an equilibriur is attained in the presence of the two chlorides, and also, in al probability, of pinene hydrochloride. Camphene hydrochlorid and *iso*bornyl chloride therefore behave as desmotropic substances and this discovery gives the explanation of the transition from th camphor to the camphene series, and vice versa. The formatio of *iso*bornyl esters from camphene occurs through isomerisation c the camphene hydrate esters primarily formed. The formation c camphene from pinene hydrochloride, *iso*bornyl chloride, and othe *iso*bornyl esters, initially obtained by the action of acidic agent on *iso*borneol takes place after previous transformation of thes

substances into camphene hydrochloride or other camphene hydrate esters:



The change, *iso*borneol ⇌ camphene, is thus closely analogous to the so-called retro-pinacoline transformation (Tiffeneau, A., 1908, i, 117), but the mechanism of the action is not fully elucidated. Most probably it consists of intramolecular atomic displacements, that is, a direct exchange of position between the alkyl radicle and the halogen atom, since it is otherwise difficult to explain the analogous change observed with tertiary alcohols and their esters.

Finally, it has been observed that the camphene obtained from optically active or inactive *iso*borneol is invariably inactive, and the same is generally true for *iso*borneol prepared from camphene. This fact was easily explicable on the assumption that symmetrical tricyclene is intermediately formed, but this hypothesis is no longer tenable. Possibly the desmotropic nature of the *iso*bornyl and camphene hydrate esters is in itself sufficient explanation of the observed racemisation, but it appears more probable that, in addition to the main reaction, *iso*borneol ⇌ camphene hydrate ⇌ camphene, a subsidiary reversible change, camphene hydrate ⇌ tricyclene, is also involved, in which racemisation occurs. Since this is caused by the presence of acids, it would therefore be expected that transformations of *iso*borneol into camphene, and vice versa, which take place in the absence of acids, would lead to optically active products. This seems actually to be the case, since active *iso*borneol has been prepared by the action of cold formic or acetic acid on camphene in the absence of mineral acid, whilst the possibility of preparing active camphene from *iso*borneol appears to be guaranteed by Ipatiev's conversion of optically active *iso*borneol and borneol into active *iso*camphane. H. W.

Chinese Pine Resin and its Essential Oil. YEINOSUKE SHINOSAKI and TETSUIJ ONO (*J. Chem. Ind. Tokyo*, 1920, **23**, 45—56).—Pine resin obtained from Wen-Chow, China, contained 8·15% of an essential oil, D^{15} 0·8670, n_D^{20} 1·4711, $[\alpha]_D$ −31·41°, which contained 85% of α-pinene, a trace of dipentene, and 11% of a tricyclic *sesquiterpene*, $C_{15}H_{24}$, b. p. 92—93°/2·5 mm., D^{15} 0·9408, D^{20} 0·9398, n_D^{20} 1·5031, $[\alpha]_D$ +47·311° in ether, which was isolated as the *monohydrochloride*, needles, m. p. 58—59°, by passing hydrogen chloride into an ethereal solution of the fraction of the essential oil, b. p. 90—105°/2·5 mm.

CHEMICAL ABSTRACTS.

Glucosides. VII. Constitution of Amygdalin. P. KARRER, C. NÄGELI, and L. LANG (*Helv. Chim. Acta*, 1920, **3**, 573—583. Compare this vol., i, 370).—The object of the experiments here

described was to ascertain if the still unknown disaccharide amygdalin is identical with cellobiose. It has been already sho (A., 1919, i, 594; this vol., i, 370, 395) that the silver salts α-hydroxy- or o-hydroxy-carboxylic acids react with acetylbron glucose, giving the acetylated glucosides and esters of th hydroxy-acids. Tetra-acetylglucosidomandelic acid, obtained this way from mandelic acid, has now been converted by the acti of phosphorus pentachloride into β-tetra-acetyl-*d*-glucosido- mandelic acid chloride, which, with the calculated quantity of d ammonia, gives the corresponding amide. These reactions ha been carried out with the inactive mandelic acid residue; t further conversion of the amide into the mandelonitrile glucosi by dehydration and deacetylation has not been proceeded with, Fischer has shown it to be possible with the active tetra-acet glucosidomandelic acid amides.

Attempts have been made to apply these methods to the p paration of mandelonitrile celloside. The interaction of inacti silver mandelate and acetobromocellobiose does, indeed, yie hepta-acetylcellosidomandelic acid, but the yield is very small, that this reaction depends more on the nature of the halogenat compound than on that of the complex silver salt; the smallne of the yield renders it impossible to convert the acid into t corresponding acid chloride and amide. Since, however, hept acetylcellosidomandelic acid is not identical with hepta-acet amygdalinic acid, it follows that the non-acetylated acids are n identical, and that the sugar of amygdalin cannot be cellobios the β-glucosidic nature of the union of the disaccharide in the tv cases is shown by the fact that hydrolysis is effected by emulsin either case.

Unsuccessful attempts have been made to induce ethyl mandela and acetobromocellobiose to react, with formation of ethyl hept acetylcellosidomandelate. Hepta-acetylethylcelloside may, ho ever, be obtained from acetobromocellobiose, alcohol, and silv oxide, and, on hydrolysis, yields ethylcelloside, which is the fir alkylcelloside known in the crystalline and pure condition (co pare Skraup and König, A., 1901, i, 370; 1902, i, 135).

β-Tetra-acetyl-d-*glucosido*-dl-*mandeloyl chloride*,

$$COCl\cdot CHPh\cdot O\cdot C_6H_7O_5Ac_4,$$

forms aggregates of concentric, colourless needles, m. p. 117—119 The corresponding *amide*, $NH_2\cdot CO\cdot CHPh\cdot O\cdot C_6H_7O_5Ac_4$, crysta lises in aggregates of colourless, concentric needles, m. p. belo 100° after previous sintering.

Hepta-acetylcellosido-dl-*mandelic acid*,

$$CO_2H\cdot CHPh\cdot O\cdot C_{12}H_{14}O_{10}Ac_7,$$

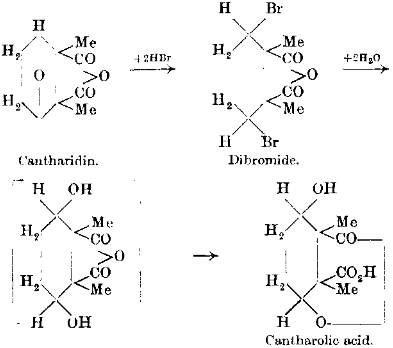
forms crystals, m. p. 179—182°, $[\alpha]_D$ about −44°, and does n reduce Fehling's solution.

Hepta-acetylethylcelloside, $C_{12}H_{14}O_{10}Ac_7\cdot OEt$, crystallises i long, white needles, m. p. 184°, $[\alpha]_D$ −24·76° (in chloroform), an reduces Fehling's solution slightly, possibly owing to sligh contamination.

Ethylcelloside, $C_{12}H_{21}O_{10}\cdot OEt$, is hygroscopic, reduces Fehling's solution in the hot, has $[\alpha]_D$ −9·55°, and yields the hepta-acetyl derivative on acetylation. T. H. P.

The Influence of the Structure of β-Glucosides on the Action of Emulsin. EMIL FISCHER (*Zeitsch. physiol. Chem.*, 1919, 176—202).—The action of emulsin on glucosides of glycollic acid, α-hydroxybutyric acid, mandelic acid, amygdalic acid, cellosidoglycollic acid, their salts, esters, amides, and nitriles, was investigated. The glucosidomandelic acid was prepared from the tetra-acetate of the ethyl ester with baryta, and the glucosido-*d*-mandelic acid was extracted from the glucosides of *d*- and *l*-mandelic acid mixture as the quinine salt. The glucosido-*d*-mandelic acid was also extracted as the cinchonine salt from the amygdalic acid mixture. *Cellosidoglycollic acid* was prepared as follows. Hepta-acetylcellosidoglycollic ester was dissolved with crystalline barium hydroxide in water, and the solution kept for one and a-half to two days at the ordinary temperature. The excess of barium was then removed with sulphuric acid, and the cellosidoglycollic acid precipitated as the lead salt, from which, by treatment with hydrogen sulphide, the free acid, $C_{14}H_{24}O_{13}$, decomp. 195°, α_D^{20} −25·12—25·65°, was obtained. The free acids were scarcely affected by small quantities of emulsin. The amides, the esters, and the nitriles were more easily hydrolysed than the other derivatives. The derivatives of glucosido-α-hydroxy*iso*butyric acid were resistant. The salts and the amide of *d*-mandelic acid, in contradistinction to the *l*-compounds, were not attacked by the enzyme; the methyl ester and nitriles of both, on the other hand, were attacked. A half of the theoretical quantity of dextrose was obtained by the emulsin hydrolysis of *d*-amygdalic acid. The nitrile of cellosidoglycollic acid, unlike the nitrile of glucosidoglycollic acid, was hydrolysed into dextrose and hydrocyanic acid. In general, it may be concluded that glucosides of phenols and phenolcarboxylic acids are degraded with greater ease than glucosides of the aliphatic alcohols and acids of a similar structure. S. S. Z.

Cantharidin. IX. Cantharolic Acid. J. GADAMER (*Arch. Pharm.*, 1920, **258**, 171—182. Compare A., 1915, i, 432).—Cantharolic acid is isolated as a by-product from the substances formed by the action of hydrogen bromide in glacial acetic acid solution on cantharidin; it occurs in the portion which is insoluble in ether, together with unchanged cantharidin and cantharic acid, from the latter of which it is separated by taking advantage of its very sparing solubility in boiling alcohol. It is an unsymmetrical, monobasic acid containing a lactone group and a free hydroxyl radicle. Its structure and genetic relationships are indicated by the scheme:



Cantharolic acid crystallises in shining rhombs, m. p. 254—256° to 258—260° (decomp.), according to the rate of heating. It is very stable towards alkaline permanganate. It behaves towards alkali as a monobasic acid. The presence of the lactone ring is demonstrated in the usual manner, and fission is found to be more complete than in the case of cantharic acid, but even here the process is complicated by the partial decomposition of the acid by excess of alkali. The hydroxyl group could not be detected by phosphorus trichloride, but the acid is converted by cold concentrated sulphuric acid into the *sulphuric* ester, which was isolated in the form of the *barium* salt, $C_{10}H_{12}O_8SBa,3H_2O$. The free substance was not obtained, since in aqueous solution it somewhat readily undergoes autohydrolysis, with the production of cantharolic acid; the crude material could be resolved into its optical antipodes by brucine in aqueous solution, thus yielding *brucine* l-*cantharolic acid sulphate*, $C_{10}H_{14}O_8S,2C_{23}H_{26}O_4N_2,7H_2O$, very slender needles, and *brucine* d-*cantharolic acid sulphate*, $C_{10}H_{14}O_8S,2C_{23}H_{26}O_4N_2,3H_2O$, coarse, plate-like needles. The brucine salts were converted into the corresponding ammonium salts, and from polarimetric analyses of the latter, the values $[\alpha]_D$ −67·2° and +67·9° are calculated for the free acids in aqueous solution. Hydrolysis of the acids occurs slowly in boiling aqueous solution, but the cantharolic acid produced is almost completely racemised, the effect appearing, however, not to be due to the protracted exposure to a somewhat high temperature. Cantharolic acid is converted by hot concentrated sulphuric acid into cantharic acid.

The resolution of *r*-cantharolic acid has also been attempted by the fractional crystallisation of the brucine salt from water; the

nost highly active acid obtained had $[\alpha]_D$ $-31{\cdot}25°$ in aqueous solu-ion, *m. p.* 260—263° (decomp.). The resolution is remarkable n that the salts only separate when the concentrated solutions are varmed, thus probably indicating the existence of a soluble ıydrated and sparingly soluble anhydrous form of the salts, and, urther, in that all the fractions yield exclusively lævorotatory ıcids. The explanation of the latter phenomenon is found in the act that whilst cantharolic acid itself is asymmetric in structure, ts hydrate, formed by hydrolysis of the lactone, is symmetrical. n aqueous solution, an equilibrium exists between the lactone and ıydrate, which is disturbed by the removal of a portion of the -acid as the brucine salt. A portion of the hydrate therefore asses into the *r*-acid, whilst, simultaneously, inactivation of the lissolved *d*-acid occurs through formation of the hydrate. In his manner, a complete conversion of the *r*-acid into the *l*-acid an be effected through the symmetrical hydrate. In agreement vith this explanation, it is found that *l*-cantharolic acid becomes lowly racemised in aqueous solution, and that the same process ccurs more rapidly in the presence of an excess of sodium hydr-xide. In addition to *r*-cantharolic acid, however, another ptically inactive acid is formed in the latter circumstances, and his is produced exclusively when cantharolic acid is heated with ılkali hydroxide on the water-bath. This acid is amorphous, and rields an amorphous calcium salt; analyses, taken in conjunction with its mode of formation, indicate that it is 1:2-dimethyl*cyclo*-ıexadienecarboxylic acid, but its physical properties suggest that it s a polymeride of this substance. H. W.

Picrotoxin. IX. Degradation of Picrotoxinin by Ozone. PAUL HORRMANN and HANS PRILLWITZ (*Arch. Pharm.*, 1920, **258**, 200—226).—Further insight into the constitution of picro-oxin (compare A., 1916, i, 566, 827) is afforded by the conversion f picrotoxinin by ozone into formic acid and a ketone, α-picro-oxininone, which, under the action of dilute sulphuric acid or concentrated hydrochloric acid, suffers a change similar to that of picrotoxin, and yields picrotoxinonic acid. These facts, combined with the behaviour of the substance towards nitric acid, lead the authors to the conclusion that the methylene group in picrotoxin is directly united to a ring carbon atom, $CH_2{:}C{<}\overline{\underline{R(C_{13}H_{14}O_6)}}|$.

Picrotoxinin is obtained in good yield from picrotoxin by a modification of the method described previously (Meyer and Bruger, A., 1899, i, 226; Horrmann, A., 1912, i, 709), and is converted by ozone in ethyl acetate solution into the corresponding ozonide. Fission of the latter to formic acid and *α-picrotoxininone*, $C_{14}H_{14}O_7$, is most conveniently effected by violent agitation with cold water. When rapidly crystallised from hot water, the substance separates in shining needles ($+H_2O$), and does not exhibit a sharp melting or decomposing point either in the hydrated or anhydrous condition. It has $[\alpha]_D^{17.5}$ $-10°6{\cdot}6'$ in

alcoholic solution. It behaves as a dilactone with two free hydroxyl groups. The presence of the ketonic oxygen atom is shown by the isolation of a *semicarbazone*, colourless leaflets ($+H_2O$), which, when air-dried, begins to decompose at 230°, when anhydrous at 224°, but without exhibiting a definite end-point of decomposition, and a *phenylhydrazone*, colourless, silky needles, decomp. 232—248° after discolouring at 225°. In boiling aqueous solution, α-picrotoxininone is slowly transformed into *β-picrotoxininone*, $C_{14}H_{14}O_7$, which is more conveniently prepared by heating the α-derivative under diminished pressure at 195°; this forms long, anhydrous needles, which are freely soluble in water, and decompose sharply and without melting at 252—253°. Like the α-compound, it is a dilactone with two free hydroxyl groups. It has $[\alpha]_D^{17.5}$ +83°23′ in alcoholic solution, and gives a *semicarbazone*, granular precipitate ($+H_2O$), which commences to decompose at 222°, darkens at 240°, and subsequently passes into a product, which decomposes above 300°, a *phenylhydrazone*, pale yellow precipitate, which decomposes definitely at 273° when rapidly heated, and an *oxime*, cubic crystals, which decomposes sharply at 255°.

α- and β-Picrotoxininone are converted by ice-cold $N/10$-aqueous potassium hydroxide solution into two different dicarboxylic *acids*, $C_{14}H_{18}O_9$, which, however, show little tendency to crystallise. The α-acid is characterised by its *phenylhydrazone*, yellow, amorphous precipitate, which decomposes definitely at 220°; the β-acid was analysed as the *silver* salt and as the *phenylhydrazone*, pale red needles, which decompose at 140—141°. α-Picrotoxininone is transformed by dilute methyl-alcoholic potassium hydroxide solution into amorphous substances and picrotoxinonic acid, needles, which decompose at 260°, $[\alpha]_D^{17.5}$ +101°46′ in ethyl alcohol (phenylhydrazine salt of the phenylhydrazone, pale yellow needles, decomp. 206—207°), which is identical with the product prepared by Horrmann and Wächter (A., 1916, i, 827) from the ozonide of picrotoxinic acid. The same acid is also obtained by the action of boiling dilute sulphuric acid on α- or β-picrotoxininone, or from the former by the prolonged action of cold concentrated hydrochloric acid.

Picrotoxinin is converted by cold concentrated hydrochloric acid into two substances, one of which, amounting to about 50% of the material taken, remains undissolved; analyses agree with $C_{15}H_{16}O_6$. Two of the oxygen atoms are present in a lactone group, since the substance slowly dissolves in warm potassium hydroxide solution (1 molecule), and the neutral solution yields a *silver* salt, $C_{15}H_{17}O_7Ag$, when treated with silver nitrate. Its other properties, notably its sparing solubility in practically all the usual media, and its high temperature of decomposition (above 300°), suggest its identity with picrotoxid prepared by Schmidt (A., 1884, 845) by the action of hydrogen chloride on picrotoxin in the presence of ether; attempts to prepare material for comparison by Schmidt's method were not, however, successful. It was not found possible to prepare an acetyl or benzoyl derivative,

or to estimate the number of hydroxyl groups. The second substance is isolated by extracting the acid solution with ether, or by evaporating it to dryness in a vacuum; the yield is not good, and the substance has not been obtained in the pure state. When dissolved in cold concentrated acetic acid and treated with an excess of phenylhydrazine, it gives a *diphenylhydrazone*,

$C_{30}H_{26}O_2N_4$,

pale yellow granules, decomp. 163°. H. W.

Hydrogenation of Furfuryl Alcohol and Furfuraldehyde to Tetrahydrofurfuryl Alcohol. HEINRICH WIENHAUS (*Ber.*, 1920, **53**, [*B*], 1656—1666. Compare Padoa and Ponti, A., 1907, i, 146; Bourguignon, A., 1908, i, 280; Pringsheim and Noth, this vol., i, 249).—Furfuryl alcohol is hydrogenated by Paal's method in aqueous solution and in the presence of sodium hydroxide sufficient to neutralise any liberated hydrogen chloride, or, preferably, in the undiluted condition in the presence of palladised charcoal, with the formation of *tetrahydrofurfuryl alcohol*, colourless liquid, b. p. 85—86°/26 mm., 177°/750 mm., D_{20}^{20} 1·054, D_4^{20} 1·0544, n_α^{20} 1·44933, n_D^{20} 1·45167, n_β^{20} 1·45680, n_γ^{20} 1·46138. The corresponding constants of furfuryl alcohol are b. p. 80°/21 mm., 82—83°/25 mm., 96°/45 mm., 171°/750 mm., D_{20}^{20} 1·131, D_4^{20} 1·1296, n_α^{20} 1·48108, n_D^{20} 1·48477, n_β^{20} 1·49398, n_γ^{20} 1·50192. The tetrahydro-alcohol does not decolorise bromine dissolved in water or light petroleum, is not rapidly oxidised by dilute permanganate solution, and does not colour a pine shaving moistened with concentrated hydrochloric acid. Furfuryl alcohol and its tetrahydro-derivative are markedly hygroscopic. The latter is most readily identified by esterification with pyruvic acid at 100° during two hours, fractionation of the product, and conversion of the crude ester into its *semicarbazone*,

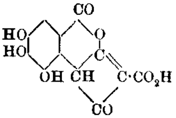
$C_4H_7O\cdot CH_2\cdot O\cdot CO\cdot CMe:N\cdot NH\cdot CO\cdot NH_2$,

colourless leaflets, m. p. 184—186°; a similar method cannot be used with furfuryl alcohol, since the mixture is rapidly transformed, with considerable development of heat, into a dark green, plastic mass. Tetrahydrofurfuryl alcohol gives a *phenylurethane*, small crystals, m. p. 61° (the corresponding *compound* of furfuryl alcohol crystallises in colourless needles, m. p. 45°); and a *diphenylurethane*, m. p. 81°.

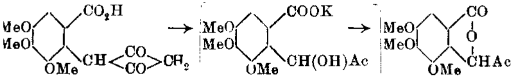
Hydrogenation of furfuraldehyde in the presence of palladised charcoal and without solvent leads chiefly to the formation of tetrahydrofurfuryl alcohol. H. W.

Galloflavin. J. HERZIG (*Annalen*, 1920, **421**, 247—282).—Tetramethylgalloflavin readily loses one methoxy-group under the influence of alkali hydroxides, and passes into trimethyl*iso*galloflavin, which has been shown to contain a carboxyl group and a lactone ring. It has now been found possible to degrade the substance by a series of comparatively simple reactions to 3:4:5-

trimethoxyphthalide, $C_6H(OMe)_3{<}^{CO-}_{CH_2}{>}O$ (compare Bargellini and Molina, A., 1912, i, 773), and thus to prove the presence of the group $C_6H(OH)_3{<}^{CO}_{C-}{>}O$ in *iso*galloflavin. After making allowance for the known presence of the carboxyl group, the residue, C_3HO, remains, which is accounted for by the existence of another ring, thus leading to the annexed formula for *iso*galloflavin.



[With Elisabeth Eyweling and Hedwig Brunner.]—Trimethyl*iso*galloflavin decomposes when distilled into carbon dioxide, and a substance, $C_{11}H_3O_3(OMe)_3$, which does not react with diazomethane or acetylating agents, and in which the lactone ring is only shown to be present with difficulty; under definite conditions of successive treatment with methyl-alcoholic aqueous potassium hydroxide solution and acid, it is possible to convert it into the *substance* (I), m. p. 74—77°; the latter is converted by the further action of alkali hydroxide and potassium formate into a *product* (II), m. p. 134—136°, and this substance is further transformed by alkali into 3:4:5-trimethoxyphthalide and potassium acetate.



(I.) (II.)

The possibility of using the tetramethyl*iso*galloflavincarboxylic acid, m. p. 132—135° (compare A., 1910, i, 676), as initial material for the study of the degradation of *iso*galloflavin has been investigated, but its method of preparation is too cumbersome for this purpose; its *methyl* ester has m. p. 53—55°.

The action of zinc dust and aqueous potassium hydroxide solution on *iso*galloflavin leads to the formation of the two acids, $C_{12}H_{10}O_7$ and $C_{10}H_8O_5$.

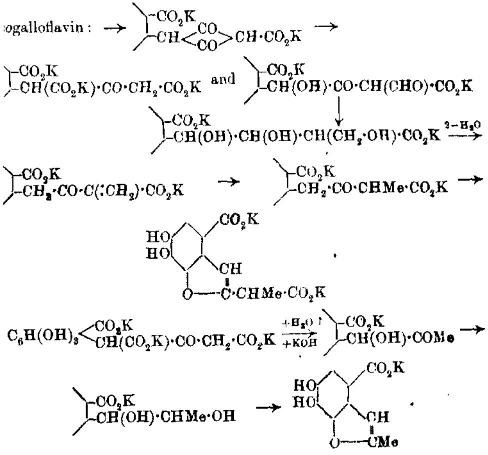
[With Franz Schaffer.]—The dihydroxy-dicarboxylic acid, $C_{12}H_{10}O_7$, silvery leaflets, m. p. 191—194° (decomp.), which is readily oxidised in aqueous solution, is characterised by its conversion by diazomethane into a *tetramethyl* derivative, m. p. 101—103°, which is hydrolysed to the corresponding *dimethoxydicarboxylic acid*, m. p. 200—203°; the latter is in part unchanged by distillation under greatly reduced pressure, and in part transformed into the *monocarboxylic acid*,

$$C_{10}H_7O(OMe)_2\cdot CO_2H,$$

m. p. 132—135° (*methyl* ester, oil). The dicarboxylic acid is unaffected by acetic anhydride, sodium acetate, and zinc dust. The acid, m. p. 191—194°, is converted by methyl-alcoholic hydrogen chloride into the *methyl* ester, $C_{10}H_6O(OH)_2(CO_2Me)_2$, m. p.

›3—156°, which yields the corresponding *diacetyl* derivative, . p. 71—73°. The dimethoxydicarboxylic acid is unaffected by *nc and potassium hydroxide solution*, by the latter alone under ·essure, and at elevated temperature by treatment with sulphuric ·id, or by oxidation with chromic acid.

[With LUDMILLA PARNAS.]—The acid, $C_{10}H_8O_5$, could not be olated in the pure condition by reason of its very ready oxidisa- lity in solution; the following series of derivatives, however, roves it to be a dihydroxymonocarboxylic acid. *Trimethyl com- ound* (from the acid and methyl sulphate in the presence of ›dium hydroxide), colourless platelets, m. p. 101—103°, which is ydrolysed to the corresponding *acid*, $C_9H_5O(OMe)_2{\cdot}CO_2H$, m. p. 35—188°, which distils unchanged under diminished pressure; *ethyl* ester, $C_9H_5O(OH)_2{\cdot}CO_2Me$ (from the crude acid and ›ethyl-alcoholic hydrogen chloride), which is very difficult to urify, has m. p. 184—190°, and yields a *diacetyl* derivative, m. p.)9—112°. The production of these acids is represented by the :hemes:

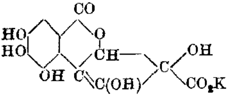


The action of zinc dust and potassium hydroxide on galloflavin proceeds in the same manner, but the yields of the reaction products are much smaller. Attempts to convert the acid $C_{12}H_{10}O_7$ into $C_{10}H_8O_5$ by prolonging the action of zinc and

potassium hydroxide on *iso*galloflavin or on the dihydroxydicarboxylic acid did not lead to the desired result.

[With KARL TRENKLE, MARIANNE SCHLEIFFER, and ELISABETH EYWELING.]—The action of acetic anhydride, sodium acetate, and zinc dust on *iso*galloflavin and its derivatives follows a somewhat complicated course. In these circumstances, *iso*galloflavin itself (which has been shown previously to give a normal triacetyl derivative with acetic anhydride and sodium acetate) yields a *tetraacetyl* compound, m. p. 203—206° (decomp.) after becoming discoloured from about 180°, and the same substance can also be prepared from triacetyl*iso*galloflavin in similar circumstances. Similarly, trimethyl*iso*galloflavin yields *acetyltrimethylisogalloflavin*, long, colourless needles, m. p. 138—140°. On the other hand, the methyl esters of trimethyl- and triacetyl-*iso*galloflavin are unchanged by this treatment, for which the presence of a free carboxyl group appears essential. The exact mechanism of the reaction has not been fully elucidated. Carbon dioxide is certainly eliminated during the process, and it appears probable that the acetyl group takes the place of the carboxyl group; on the other hand, since the action only occurs in the presence of zinc dust (acetic anhydride and zinc acetate do not even cause acetylation of the free hydroxyl groups of *iso*galloflavin), it is possible that the carbonyl group adjacent to the carboxyl radicle is reduced, and the secondary alcoholic group is then acetylated. Attempts to gain further insight into the action by a study of analogous substances do not afford much general information. Thus, 3:4:5-trimethoxyphthalidecarboxylic acid gave an almost quantitative yield of the corresponding phthalide, both in the presence and absence of zinc dust, whilst benzilic acid yielded small quantities of $\beta\beta$-diphenylpropionic acid. With 5:6-dimethoxyphthalidecarboxylic acid, a more complex change occurs, which does not give rise to the formation of the phthalide.

The presence of a carboxyl group in *iso*galloflavin is clearly demonstrated by its direct conversion into the methyl ester, m. p. 300—305° after previous darkening by methyl-alcoholic hydrogen chloride. In similar circumstances, galloflavin is absolutely unaffected. The conversion of galloflavin into *iso*galloflavin appears to be due to a change of the type of the benzilic acid transformation brought about in the five-membered ring of the former by potassium hydroxide,



yielding the intermediate product (annexed formula), which passes, by loss of water, into *iso*galloflavin. H. W.

Ring Formation. KARL VON AUWERS (*Annalen*, 1920, **421**, 1—118).—[With ELISABETH LÄMMERHIRT.]—In view of the unexpected formation of 3:6-dimethyl-2:3-dihydro-1:4-benzopyrone, m. p. 34—35° (semicarbazone, m. p. 232°), by the action of diethyl-

niline on *m*-*a*-bromo*iso*butyryl-*p*-cresol (A., 1917, i, 277), the con-
stitution of the product has been rigidly proved, not only synthetically (*loc. cit.*), but also by its conversion through the *bromo*-derivative, crystals, m. p. 70—71° (obtained by bromin-tion in carbon disulphide solution), *into 3:6-dimethylchromone* [*3:6-dimethyl*-1:4-*benzopyrone*], $C_6H_3Me<\begin{smallmatrix}CO\cdot CMe \\ \| \\ C—CH\end{smallmatrix}$, colourless eedles, m. p. 61—62°, b. p. 299—301°/atm., or 165—168°/5 mm., by means of boiling dimethylaniline. 3:6-Dimethyl-1:4-enzopyrone, which yields *m*-propionyl-*p*-cresol and formic acid by oiling with alcoholic sodium ethoxide, has also been prepared by ondensing *m*-propionyl-*p*-cresol and ethyl oxalate by means of odium, heating the oily condensation product,

$$OH\cdot C_6H_3Me\cdot CO\cdot CHMe\cdot CO\cdot CO_2Et,$$

ith concentrated hydrochloric acid, and eliminating carbon ioxide from the resulting 3:6-dimethyl-1:4-benzopyrone-2-carb-xylic acid.

Contrary to the statement of Auwers and Krollpfeiffer (A., 915, i, 442), 3-bromo-6-methyl-2:3-dihydro-1:4-benzopyrone is onverted into 6-methyl-1:4-benzopyrone by boiling with dimethyl-niline.

The *conversion of m-a-bromoisobutyryl-p-*cresol into 3:6-di-nethyl-2:3-dihydro-1:4-benzopyrone (see above) must involve the ntermediate formation of the unsaturated ketone,

$$OH\cdot C_6H_3Me\cdot CO\cdot CMe\!:\!CH_2.$$

n order to ascertain whether the conversion of such unsaturated etones into benzopyrones is a general reaction, the condensation f *p*-tolyl methyl ether and crotonyl chloride by means of luminium chloride has been examined. The reaction is compli-ated, and one or more of five different products may be obtained, ccording to the experimental conditions. It has been established, owever, that if the ethereal solution of the initial condensation roduct is repeatedly shaken with aqueous sodium hydroxide, three roducts are obtained: (1) the methyl ether of *m*-crotonyl-*p*-resol, $OMe\cdot C_6H_3Me\cdot CO\cdot CH\!:\!CHMe$ (only isolated as the disemi-arbazide *derivative*,

$$OMe\cdot C_6H_3Me\cdot C[\!:\!N\cdot NH\cdot CO\cdot NH_2]\cdot CH_2\cdot CHMe\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

n. p. 205—206°), (2) *2:6-dimethyl-2:3-dihydro-1:4-benzopyrone*, n. p. 54—55° (*semicarbazone*, m. p. 203°), and (3) 7-hydroxy-3:4-imethylhydrindone, whilst if the ethereal solution is directly dis-illed under diminished pressure, the chief product is *m-crotonyl-p-cresol*, $OH\cdot C_6H_3Me\cdot CO\cdot CH\!:\!CHMe$, yellow solid, m. p. 65—66°, vhich is quantitatively converted into the isomeric 2:6-dimethyl-:3-dihydro-1:4-benzopyrone by distillation at the ordinary ressure (b. p. 277—278°), or by treatment with aqueous sodium ydroxide.

2:6-Dimethyl-2:3-dihydro-1:4-benzopyrone has been synthesised y condensing *β-chlorobutyryl chloride*, b. p. 51—53°/21 mm., vith *p*-tolyl methyl ether, and eliminating hydrogen chloride from he resulting *m-β-chlorobutyryl-p-cresol* by means of sodium

carbonate. By bromination, it yields 3-*bromo*-2 : 6-*dimethyl*-2 : 3-*dihydro*-1 : 4-*benzopyrone*, m. p. 104—105°, which is converted into 2 : 6-*dimethyl*-1 : 4-*benzopyrone*, m. p. 102—103°, by boiling with dimethylaniline; the benzopyrone has also been prepared by condensing the methyl ether of *m*-acetyl-*p*-cresol with ethyl acetate and boiling the product, $OMe\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot COMe$, with hydriodic acid.

There is little doubt that the inability of *m*-α-bromo*iso*butyryl-*p*-cresol to give a trimethylcoumaranone is due to the *gem*-dimethyl group. That this group does not hinder the formation of a 6-ring is shown by the following experiments with *p*-hydroxy-*m*-tolyl*iso*butenyl ketone. The reaction in carbon disulphide between equimolecular quantities of *p*-tolyl methyl ether and ββ-dimethylacrylyl chloride in the presence of aluminium chloride yields different products, according to the conditions. 7-*Hydroxy*-3 : 3 : 4-*trimethylhydrindone*, $OH\cdot C_6H_2Me<^{CMe_2}_{CO}>CH_2$, colourless prisms m. p. 67—68° (*sodium* derivative; *semicarbazone*, needles, m. p. 201—202°), is obtained in small quantity. When an ethereal solution of the reaction product is shaken with sodium hydroxide solution and the resulting oil is treated with semicarbazide, the *semicarbazone*, m. p. 199—200°, of 2 : 2 : 6-trimethyl-2 : 3-dihydro-1 : 4-benzopyrone and m-β-*semicarbazido*iso*valeryl*-p-*cresol*,

$$OH\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot CMe_2\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

m. p. 148—149° (to be described elsewhere), are obtained. When the reaction product is not treated with sodium hydroxide, the principal product is p-*hydroxy*-m-*tolyl* iso*butenyl ketone*,

$$OH\cdot C_6H_3Me\cdot CO\cdot CH{:}CMe_2,$$

sulphur-yellow prisms and needles, m. p. 50—50·5°, b. p. 159—160°/15 mm., $D_4^{53\cdot 8}$ 1·0376, n_α 1·56280, n_D 1·57187 at 53·8°. This ketone is converted into 2 : 2 : 6-trimethyl-2 : 3-dihydro-1 : 4-benzopyrone by heating at 277—278°, by boiling with diethylaniline (but not with pyridine), by treatment with dilute sodium hydroxide solution or with sodium methoxide solution, or with boiling absolute alcohol containing a few drops of concentrated hydrochloric (but not dilute sulphuric acid at the ordinary temperature) acid. It is reduced in methyl-alcoholic solution by hydrogen and colloidal palladium to p-*hydroxy*-m-*tolyl* iso*butyl ketone* (*semicarbazone*, m. p. 204°), reacts additively with hydrogen chloride in cold glacial acetic acid to form p-*hydroxy*-m-*tolyl* β-*chloro*iso*butyl ketone*, $OH\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot CMe_2Cl$, prisms, m. p. 53—55° (which is smoothly converted into 2 : 2 : 6-trimethyl-2 : 3-dihydro-1 : 4-benzopyrone by sodium hydroxide solution), and by bromination in cold carbon disulphide solution yields the *dibromide*, $OH\cdot C_6H_3Me\cdot CO\cdot CHBr\cdot CMe_2Br$, faintly yellow needles m. p. 70—71°; this is converted by dilute sodium hydroxide solution into 3-*bromo*-2 : 2 : 6-*trimethyl*-2 : 3-*dihydro*-1 : 4-*benzopyrone*, m. p. 75—76°, which is also obtained by the careful bromination of the trimethylchromanone.

The section closes with a comparison of the physical properties

of 6-methyl-, 3:6- and 2:6-dimethyl-, and 2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrones, and of the ease of formation of their semicarbazones, oximes, *p*-nitrophenylhydrazones, 3-bromo- and 3:3-dibromo-derivatives; the conversion of the bromo-derivatives into benzopyrones, of the dihydrobenzopyrones into dihydrobenzopyranols by Grignard reagents, and of the last into benzopyrens, is also described. Curiously enough, 2:2:6-trimethyldihydrobenzopyrone and magnesium methyl iodide in ethereal solution give visible signs of interaction, but, on working up the product, the unchanged trimethyldihydrobenzopyrone is obtained. 3:4:6-*Trimethyl*-2:3-*dihydro*-1:4-*benzopyranol*,

$$C_6H_3Me{<}\begin{matrix}CMe(OH)\cdot CHMe\\ O\text{———————}CH_2\end{matrix},$$

stout prisms, m. p. 123—124°, is converted by phosphoric oxide on the water-bath into 3:4:6-*trimethyl*-Δ^3-*benzopyren*,

$$C_6H_3Me{<}\begin{matrix}CMe{:}CMe\\ O\text{———}CH_2\end{matrix},$$

b. p. 135—136°/13 mm. 2:4:6-*Trimethyldihydrobenzopyran*-4-*ol*, prisms, m. p. 89—90·5°, and 2:4:6-*trimethyl*-Δ^3-*benzopyren*, b. p. 138·5—139·5°/25 mm., have been prepared.

[With H. Schütte.]—Since the facility of formation of coumaranones is increased by meta-substituents in the phenolic portion of the molecule (Auwers and Pohl, A., 1914, i, 981), 3:5-dimethylcoumaran-2-one, for example, being the most easily formed and the stablest of the coumaranones, it becomes of interest to ascertain whether the meta-substituting methyl groups or the *gem*-dimethyl group in 6-α-bromo*iso*butyryl-*m*-5-xylenol exercises the predominating influence when this compound is treated with reagents for the removal of hydrogen bromide; in the latter case, a tertiary alcohol would be expected, in the former a coumaranone or a dihydrobenzopyrone. The only product obtained when equal molecular quantities of *m*-5-xylyl methyl ether and α-bromo*iso*butyryl bromide are heated with aluminium chloride in carbon disulphide solution is 1:1:3:5-*tetramethylcoumaran*-2-*one*, colourless needles, m. p. 41—42°, b. p. 130°/12 mm., $D_4^{18\cdot2}$ 1·0620, D_4^{20} 1·060, n_α 1·53765, n_D 1·54359, n_β 1·56110, n_γ 1·57820 at 18·2°, which has also been prepared by methylating 1:3:5-trimethylcoumaranone with sodamide and methyl iodide in dry ethereal solution. The compound does not react with semicarbazide or *p*-nitrophenylhydrazine, and is only slowly attacked by bromine in carbon disulphide, yielding 4-*bromo*-1:1:3:5-*tetramethylcoumaranone*, silky needles, m. p. 74·5°, which has also been prepared by the interaction of 2-*bromo*-m-5-*xylyl methyl ether*, m. p. 24—25°, b. p. 137—139°/20 mm. (obtained by methylating the corresponding xylenol with methyl sulphate), and α-bromo*iso*butyryl bromide in the presence of aluminium chloride. 4:6-*Dibromo*-1:1:3:5-*tetramethylcoumaranone*, colourless needles, m. p. 151—152°, is

obtained by warming 1:1:3:5-tetramethylcoumaranone wit bromine in glacial acetic acid solution, or by treating it wit bromine and 2% of aluminium.

The reaction between *m*-5-xylyl methyl ether, *iso*butyryl chloride and aluminium chloride in carbon disulphide leads to the forn ation of 5-*hydroxy*-m-6-*xylyl* iso*propyl ketone*,

$$OH\cdot C_6H_2Me_2\cdot COPr^{\beta},$$

stout prisms, m. p. 93—94°, b. p. 160—165°/24 mm., which doe not form an oxime or a semicarbazone, but yields a p-*nitrophenyl hydrazone*, yellow leaflets, m. p. 181—182°, and is converted b bromine in glacial acetic acid, according to the conditions, int 2-*bromo*-5-*hydroxy*-m-6-*xylyl* β-*bromo*iso*propyl ketone*,

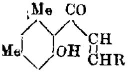
$$OH\cdot C_6HMe_2Br\cdot CO\cdot CMe_2Br,$$

stout prisms, m. p. 128—129°, or 2:4-*dibromo*-5-*hydroxy*-m-6 *xylyl* β-*bromo*iso*propyl ketone*, stout needles, m. p. 154°, each o which is smoothly converted into the corresponding brominate coumaranone by aqueous sodium hydroxide or boiling diethyl aniline.

m-5-Xylyl methyl ether, butyryl chloride, and aluminiur chloride react in carbon disulphide solution to give 5-*hydroxy* m-6-*xylyl propyl ketone*, $OH\cdot C_6H_2Me_2\cdot COPr^{a}$, stout prisms, m. p 58—59°, and its *methyl* ether, b. p. 162°/16 mm., the latter bein obtained even when an excess of aluminium chloride is used. Th hydroxy-ketone does not react with hydroxylamine or semicarb azide, but forms a p-*nitrophenylhydrazone*, yellow crystals, m. p 162—162·5°. The *acetate*, b. p. 173—175°/12 mm., by treatmen with bromine (1 mol.) in carbon disulphide, yields 5-*acetoxy* m-6-*xylyl* α-*bromopropyl ketone*, $OAc\cdot C_6H_2Me_2\cdot CO\cdot CHBrEt$, m. p 36·5—38·5°, which is converted by hot aqueous-alcoholic sodiun hydroxide into 3:5-dimethyl-1-ethylcoumaranone (see followin section). When 5-hydroxy-*m*-6-xylyl propyl ketone is brominate in the same way as its acetate, the product is 2-*bromo*-5-*hydroxy* m-6-*xylyl propyl ketone*, leaflets, m. p. 108—109°, but when tw and three molecules of bromine are used, the product is 2-*bromo* 5-*hydroxy*-m-6-*xylyl* α-*bromopropyl ketone*, m. p. 112·5—113·5° and 2:4-*dibromo*-5-*hydroxy*-m-6-*xylyl* α-*bromopropyl keton* colourless needles, m. p. 124—125°, respectively. 2-Bromo-5 hydroxy-*m*-6-xylyl propyl ketone has also been prepared fron 2-bromo-*m*-5-xylyl methyl ether, butyryl chloride, and aluminiur chloride, a remarkable by-product of the reaction being 2:4-*di bromo*-m-5-*xylyl methyl ether*, m. p. 108—109° (also prepared b methylating the dibromoxylenol).

4-*Bromo*-3:5-*dimethyl*-1-*ethylcoumaranone*, flattened prisms m. p. 60—61°, is smoothly obtained by treating an acetone solu tion of 2-bromo-5-hydroxy-*m*-6-xylyl α-bromopropyl ketone witl aqueous sodium hydroxide; by bromination in carbon disulphide it yields 1:4-*dibromo*-3:5-*dimethyl*-1-*ethylcoumaranone*, m. p 44—45°.

[With R. Döll.]—The object of this section is to ascertai



whether unsaturated hydroxy-ketones of the annexed type yield coumaranones or dihydrobenzopyrones by treatment with ring-forming agents.

The reaction between *m*-5-xylyl methyl ether, crotonyl chloride, and aluminium chloride in carbon disulphide leads to the formation of 2:5:7-*trimethyl-2:3-dihydrobenzopyrone*, $C_6H_2Me_2<\begin{matrix}CO\cdot CH_2\\ O-CHMe\end{matrix}$, silky, needles, m. p. 66—67°, b. p. 172—174°/23 mm. (*semicarbazone*, m. p. 219—220° [decomp.]; p-*nitrophenylhydrazone*, orange-red needles, m. p. 230—231°); no trace of a coumaranone could be discovered, although thorough search was made. 3:5-*Dimethyl-1-ethylcoumaranone*, b. p. 152—154°/18 mm., $D_4^{20.5}$ 1·0667, n_a 1·53689, n_D 1·54240, n_β 1·55907, n_γ 1·57403 at 20·5°, is prepared by treating *m*-5-xylyl methyl ether and α-bromobutyryl bromide with aluminium chloride in carbon disulphide solution, and shaking the resulting bromobutyroxylenol with aqueous methyl-alcoholic potassium hydroxide; the coumaranone must be purified through its *acetate*, $C_6H_2Me_2<\begin{matrix}C(OAc)\\ O\end{matrix}>CEt$, b. p. 175—179°/23 mm., obtained by digesting it with acetyl chloride. The coumaranone does not react with semicarbazide under the usual conditions, and is converted by *p*-nitrophenylhydrazine into the pp′-*dinitro-osazone* of 5-hydroxy-*m*-6-xylyl ethyl diketone, $OH\cdot C_6H_2Me_2\cdot C(:N\cdot NH\cdot C_6H_4\cdot NO_2)\cdot CEt:N\cdot NH\cdot C_6H_4\cdot NO_2$, orange-red crystals, m. p. 246°.

Under the influence of aluminium chloride, *m*-5-xylyl methyl ether and ββ-dimethylacrylyl chloride in carbon disulphide yield 2:2:5:7-*tetramethyl-2:3-dihydro-1:4-benzopyrone*, stout prisms, m. p. 71—72°, b. p. 163—166°/17 mm. (*semicarbazone*, needles, m. p. 198—199°; p-*nitrophenylhydrazone*, stout, brick-red prisms, m. p. 210—211°); absence of 3:5-*dimethyl*-1-iso*propylcoumaranone* among the by-products was not definitely ascertained. This coumaranone, b. p. 156°/20 mm., $D_4^{21.0}$ 1·0472, n_a 1·53396, n_D 1·53955, n_β 1·55610, n_γ 1·57256 at 21·0°, was prepared from *m*-5-xylyl methyl ether and α-bromo*iso*valeryl bromide in the usual way.

By warming an alcoholic solution of benzaldehyde and 4-hydroxy-*m*-tolyl methyl ketone with 50% sodium hydroxide at 50° for many hours, and acidifying the resulting sodium salt, 4-*hydroxy-m-tolyl styryl ketone*, $OH\cdot C_6H_3Me\cdot CO\cdot CH:CHPh$, stout, orange, apparently rhombic crystals, m. p. 111°, is obtained, which evidently is not convertible into a bicyclic compound by alkali; by variations from the conditions of preparation mentioned above, however, 6-methylflavonone is formed in place of, or together with, the ketone. The ketone forms a *dibromide*, pale yellow, hexagonal prisms, m. p. 151—152°, which in warm alcoholic solution is easily converted into 3-*bromo-6-methylflavanone*, colourless leaflets, m. p. 130°, by *N*/10-sodium hydroxide.

The conversion of an *o*-hydroxy-ketone with an unsaturated side-:hain into a bicyclic compound by alkali may be represented by .he scheme:

$$R<\begin{matrix}CO—CH \\ OH \quad CHR'\end{matrix} \rightarrow R<\begin{matrix}CO—CH_2 \\ OH \quad CHR'\cdot OH\end{matrix} \rightarrow R<\begin{matrix}CO\cdot CH_2 \\ O—CHR'\end{matrix},$$

he intermediate compound being unstable in the presence of .lkali. An unsuccessful attempt to prepare such a compound has ›een made. 4-*Hydroxy*-m-*tolyl β-chloropropyl ketone*,

$$OH\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot CHMeCl,$$

olourless needles, m. p. 66—67°, prepared from the unsaturated :etone and hydrogen chloride in glacial acetic acid at 0°, forms an *cetate*, prisms, m. p. 86—87° (which is best prepared, however, ›y heating the unsaturated ketone with acetyl chloride at 100° in . sealed tube), in which, however, all attempts to replace the hlorine atom by an acetoxy-group failed.

The paper closes with a review of the most important results ecorded in the three preceding sections and in thirteen papers ›ublished during the last six years in connexion with the form-ition of coumaranones, dihydrobenzopyrones, and hydroxy-ıydrindones. C. S.

The Chelidonium Alkaloids. II. [Quantitative Estima-ion of the Methylenedioxy-group in Alkaloids.] [. GADAMER (*Arch. Pharm.*, 1920, **258**, 148—167. Compare this 7ol., i, 75).—The first part of the communication is devoted to a 'ull description of the experimental evidence on which the author ›ases his formula for *allo*cryptopine, a preliminary announcement ›f which has been made previously (*loc. cit.*). *allo*Cryptopine is onverted by phosphoryl chloride into *isoallo*cryptopine chloride, olourless needles, m. p. 200—202°, which immediately develop a lark violet coloration with concentrated sulphuric acid, and this s identical in all respects (the mixture has m. p. 199—202°) with .he product obtained by the action of potassium chloride on di-ıydroberberine methosulphate; further, *isoallo*cryptopine chloride s transformed by silver methyl sulphate into a product, m. p. .95—198°, which is identical with dihydroberberine metho-ulphate, m. p. 197—200° (Perkin, T., 1916, **109**, 834). Again, *llo*cryptopine is reduced by sodium amalgam in sulphuric acid olution to dihydro*allo*cryptopine, m. p. 167—168°, which is con-'erted by phosphoryl chloride into *iso*dihydro*allo*cryptopine :hloride, m. p. 248—250° (decomp.), which is identical with tetra-ıydroberberine methochloride, m. p. 249—251° (decomp.), and :he identity of the compounds is confirmed by comparison of their ›romides.

When the O-acetyl derivative of chelidonine is oxidised with nercuric acetate, a colourless, non-basic substance is obtained, vhich, particularly in acid solution, gradually acquires an intensely 'eddish-yellow coloration and basic properties. Its behaviour is .hus strikingly analogous to that of dihydrochelerythrine described

by Karrer (A., 1917, i, 349). Chelerythrine itself can, however, scarcely be directly related to chelidonine, but appears to be closely allied to α-homochelidonine. A preliminary examination of the subject reveals the following facts. Chelerythrine contains two methoxy- and one *methylenedioxy-groups*. A *keto-group cannot*, therefore, be present, and the reactions considered by Karrer to be due to the carbonyl group are to be regarded as occurring in the same manner as with cotarnine and berberine. Karrer's assumption of the elimination of a chain, C_5H_5O, in the formation of chelalbin compounds is highly improbable, and in this connexion it is to be noted that berberine yields additive compounds with Grignard's reagents. In its salts, chelerythrine is a quaternary base, the properties of which are due to the nitrogen atom (and not to basic oxygen, as postulated by Karrer). The free ammonium base appears incapable of existence; when the salts are treated with alkali, it immediately passes into the colourless carbinol base. It is extremely probable that an analogue of chelerythrine exists in nature which forms a chloride,

$$C_{20}H_{14}O_4NCl,$$

differing from sanguinarine chloride, $C_{20}H_{16}O_4NCl$, by containing two less hydrogen atoms, and it appears to have been occasionally mistaken for the latter. The substance ultimately obtained from O-acetylhomochelidonine has m. p. 160—162°, and is identical with dihydrochelerythrine obtained by Karrer's method from an authentic specimen of chelerythine (Karrer gives m. p. 143—144°, but his product is shown to be contaminated with impurities present in Merck's preparation from *Sanguinaria canadensis*). *The identity of the products is further established* by the fact that the material from either source becomes oxidised on exposure to air to chelerythrine, which is identified as the cyanide, m. p. 258° (for which Karrer gives varying melting points).

[With WINTERFELD.]—Under the action of concentrated sulphuric acid, substances containing the methylenedioxy-group readily lose formaldehyde, which is capable of further condensation; its action on phloroglucinol has been adapted by Weber and Tollens to the qualitative detection and quantitative estimation of the methylenedioxy-group, and the reaction has been occasionally applied to alkaloids (see, for example, Gaebel, A., 1910, i, 502), with which, however, it does not give very definite results. The method has been investigated further, and the following process is recommended. Pure phloroglucinol (0·3 gram) is dissolved in a warm mixture of water (15 c.c.) and concentrated sulphuric acid (15 c.c.), and the weighed quantity of alkaloid dissolved in water (5 c.c.) is added. The mixture is shaken until a clear solution is obtained, and treated with concentrated sulphuric acid (10 c.c.). *The flask is closed with a funnel and heated over* wire gauze until the solution boils gently and a precipitate begins to form. It is then warmed in the water-bath at 70—80° for three hours. After twenty-four hours, the precipitate is filtered

through a Gooch crucible, washed with water (60 c.c.), dried a 100° for four hours, and weighed. The weight of phloroglucid divided by 9·857 gives the amount of methylene, CH_2. Th method has several sources of error, and should therefore b effected with differing amounts of alkaloid and occasional blanl experiments. The results are to be regarded as minimal values The markedly low values are due to the fact that the eliminate formaldehyde only combines in part with the phloroglucinol t yield an insoluble phloroglucide, whilst another portion combine with the alkaloid or with alkaloid and phloroglucinol. The basi substances naturally remain dissolved in the acid, but may h partly precipitated when the latter is diluted with water (th precipitate should therefore be thoroughly drained before washin is commenced). The frequent observation during the examinatio of the colour reactions of alkaloids with concentrated sulphuri acid, that the mixture becomes turbid on exposure to moisture (fc example, with bulbocapnine), thus receives its explanation. I general, the method is sufficiently accurate to allow a decision a to whether one or two methylenedioxy-groups are present. Tw such groups are thus shown to be contained in chelidonine, cor cavine and corycavamine, and one in corycavidine. H. W.

Chelerythrine. K. Hugo Bauer and K. Th. Hedinger (*Arc Pharm.*, 1920, **258**, 167—170).—For the preparation of th alkaloid [colourless, prismatic leaflets from alcohol (+EtOH m. p. 207°], the total alkaloids from the *Sanguinaria* root are mixe with milk of lime, the product is dried, and extracted with mixture of equal parts of ether and benzene. The alkaloids a removed from the extract with citric acid, and subsequently pr cipitated with ammonia, and again dissolved in benzene. Th residue obtained after removal of the latter is repeatedly crysta lised from ethyl alcohol. The following salts have been prepared hydrochloride, $C_{21}H_{17}O_4N,HCl,H_2O$, egg-yellow needles (compa Schmidt, König, and Tietz, A., 1893, i, 496; Fischer, A., 190 i, 742; Karrer, A., 1917, i, 349); *hydriodide*, anhydrous, dark r needles, which become pale brown at 150—160°; tartrat anhydrous, dark red crystals arranged in rosettes; *oxalate*, reddis yellow needles; *methyl sulphate*, $C_{21}H_{17}O_4N,2Me_2SO_4,3MeOH$ short, golden-yellow needles. Contrary to the observation of Tiet chelerythrine hydriodide or hydrochloride does not evolve meth iodide when treated with hydriodic acid at a temperature belo 125°, and hence the alkaloid does not contain a methoxy-grou On the other hand, evolution of methyl iodide is observed at 14 and again at 275° in the estimation of the methylimino-groups the hydriodide (at 165° and 245°, respectively, with the hydr chloride), thus indicating the presence of the NMe_2 group.

Chelerythrine absorbs two atoms of hydrogen when catalytical hydrogenated in the presence of colloidal palladium, but the pr duct has not yet been obtained in the pure state.

H. W.

Oxidation of Quinine with Hydrogen Peroxide. MAXIMILLIAN NIERENSTEIN (*Biochem. J.*, 1920, **14**, 572—573).—An examination of the oxidation products resulted only in the isolation of quitenine, although a very careful search was made for hæmoquinic acid (compare A., 1919, i, 236; this vol., ii, 456).

J. C. D.

The Transformations of Cinchonine. E. JUNGFLEISCH and E. LÉGER (*Ann. Chim.*, 1920, [ix], **14**, 59—128, 129—188).—A résumé of work already published (A., 1888, 380, 507, 612, 729, 969; 1889, 906; 1891, 1121; 1892, 222, 1253; 1893, i, 679; 1894, i, 262, 351; 1895, i, 310, 404; 1901, i, 287, 338; 1918, i, 121, 182, 232, *304*; *1919*, i, *170*, 451, 597).

W. G.

Syntheses of Inactive Ephedrine or ψ-Ephedrine. AUGUST EBERHARDT (*Arch. Pharm.*, 1920, **258**, 97—129).—Basing his experiments on the formula OH·CHPh·CHMe·NHMe proposed by Schmidt for the alkaloids, the author has succeeded in synthesising inactive ephedrine and ψ-ephedrine (which have not up to the present been obtained from the natural active bases) in such quantity that their resolution can now be studied; the method finally adopted is an improvement of that proposed by Schmidt and Calliess (A., 1911, i, 742).

Methylation of Phenyl α-Aminoethyl Ketone or Phenylaminoethylcarbinol.—Phenylaminoethylcarbinol hydrochloride is slowly converted by methyl sulphate at 100° into a *substance*, shining needles and leaflets, m. p. 244°, which appears to have the constitution indicated by the formula $\begin{array}{l}\text{CHPh·CHMe·NH}_3\\ \text{O——SO}_2\text{——O}\end{array}$, and to b analogous to the products obtained by Schmidt (A., 1914, i, 989) by the action of sulphuric acid on ephedrine and silver sulphat on ψ-ephedrine. Various attempts to methylate the free base wit methyl sulphate are described, which, however, are either com pletely unsuccessful or yield such small amounts of methylate substance that its identity cannot be established. Similarly, th action of methyl sulphate on phenyl α-aminoethyl ketone proceed very indefinitely, but does not give rise to a betaine-like deriv ative, for the formation of which the presence of a hydroxyl grou in the parent molecule appears to be necessary. Phenylamino ethylcarbinol hydrochloride is unaffected by methyl alcohol a 170—180°. The main product of the action of methyl iodide o phenyl α-aminoethyl ketone is diphenyldimethylpyrazine, needles m. p. 125°, the decomposition of the ketone proceeding far mor rapidly than its methylation; the substance is further identifie by conversion into its unstable hydrochloride, platinichloride *aurichloride*, yellow leaflets, m. p. 115°, *mercurichloride*, plate and flat needles, m. p. 193—195° after softening at 180°, and it *compound* with silver nitrate, $C_{18}H_{16}N_2,3AgNO_3$, slender, shinin needles, m. p. 247° (decomp.). Methyl iodide appears to b without action on the *acetyl* derivative of phenylaminoethyl

carbinol or on mono- or di-benzoylphenylaminoethylcarbinols [the latter has m. p. 165° instead of 162°, recorded previously (A., 1917, i. 392), and yields a *hydrochloride*, needles, m. p. 203° after previous softening]. A satisfactory methylation could not be effected by the action of formaldehyde on phenylaminoethylcarbinol hydrochloride. Phenyl α-aminoethyl ketone does not react readily with benzaldehyde, whilst the product obtained from phenylaminoethylcarbinol under similar conditions could not be caused to crystallise; treatment of the crude product with methyl iodide, however, gave a small quantity of phenylmethylaminoethylcarbinol hydriodide, plates, m. p. 169—170°, which was further characterised by its conversion into the corresponding aurichloride, m. p. 111·5° after softening at 108°.

Syntheses from Methylamine and Phenyl Bromoethyl Ketone.—α-Methylaminopropiophenone is more conveniently prepared from methylamine and phenyl bromoethyl ketone in absolute alcoholic solution than in benzene solution, as previously described (A., 1915, i. 834), and is isolated as the hydrochloride; the latter is readily reduced by hydrogen under slight pressure in the presence of palladinised charcoal to phenyl-α-methylaminoethylcarbinol, m. p. 114°, the process being much preferable to the reduction with sodium amalgam described previously (*loc. cit.*); the hydrochloride thus obtained differs from the former compound in its higher melting point, 187° instead of 181—182°, and its more sparing solubility. It is further found that, in addition to the compound, m. p. 114°, an isomeric substance, slender needles, m. p. 76°, also exists, and these are provisionally termed base *B* and base *A*. They yield, respectively, the *hydrochlorides*, readily soluble, ill-defined crystals, m. p. 158—161°, and colourless, rhombic plates, m. p. 187°; *aurichlorides*, flat needles, m. p. 115—116°, and then yellow plates or golden-yellow lamellæ, m. p. 115°; *platinichlorides*, reddish-yellow crusts, m. p. 177° (decomp.), and yellowish-red rosettes, m. p. 183° (decomp.); *dibenzoyl* derivatives, coarse, colourless crystals, m. p. 118—119°, and colourless rods, m. p. 114—115°. The *acetyl* derivative from either isomeride is oily, but yields a crystalline *hydrochloride*, colourless plates, m. p. 165—167°.

The synthetic compounds, their salts, and derivatives show great similarity to the natural bases, both in appearance and melting point, which is particularly noticeable in the case of the *B*-base and ψ-ephedrine. The bases *A* and *B* exhibit an interconvertibility which is precisely similar to that of ephedrine and ψ-ephedrine. This can be partly effected by hydrochloric acid at the ordinary pressure, but more readily at higher temperature and under increased pressure, whilst the base *A* is completely converted into base *B* by acetylation—an action which is not observed during benzoylation. Transformation does not take place when base *A* is heated alone in the presence of alkali or of a number of solvents; with chloroform, the hydrochloride is formed as a result of the decomposition of the solvent. H. W.

Alkylation of Phenols with Benzenesulphonic Esters. Certain New Morphine Ethers. ZOLTÁN FÖLDI (*Ber.*, 1920, 53, [*B*], 1839—1847).—The use of arylsulphonic esters for the conversion of phenols into ethers has been recommended by Ullmann and Wenner (A., 1903, i, 407), but the optimal conditions for the reaction, and the influence on it of the presence of substituents in the phenol, do not appear to have been studied extensively. The author has therefore performed a series of experiments in which the phenol is generally dissolved in ethyl or amyl alcohol, treated with a solution of the calculated amount of sodium in one of these media, and the product is heated to boiling with the arylsulphonyl ester. The yields usually approximate to those theoretically possible, and since the alkylating agent is readily prepared (compare this vol., i, 828), the process appears capable of extended application. Alkylation occurs most readily with allyl benzenesulphonate, whilst the halogenated alkyl esters react considerably more slowly than the corresponding unsubstituted compounds. In general, it appears that the most easily saponifiable esters have the greatest alkylating action. With regard to substituents in the phenolic group, the same rule is applicable as in the case of alkylation with methyl sulphate; the presence of negative substituents hinders the reaction, but the effect is less marked with para- than with ortho-substituents.

The following ethers have not been described previously: o-*chlorophenyl allyl ether*, colourless oil, b. p. 118—120°/18 mm., D_4^{15} 1·133; *catechyl diallyl ether*, pale yellow, mobile oil, b. p. 140—145°/17 mm., 136—139°/14 mm., D_4^{15} 1·011; *catechol monoallyl ether*, pale yellow, mobile liquid, b. p. 110°/12 mm., D_4^{15} 1·091; *allylmorphine*, colourless crystals ($+\frac{1}{2}H_2O$), m. p. 67—68° [*hydrochloride* ($+1H_2O$), m. p. 128—129° when rapidly, 130—132° when slowly heated, or anhydrous, m. p. 152—153°, $[\alpha]_D^{19}$ −85·69° in aqueous solution; *hydriodide*, pale yellow, anhydrous crystals, m. p. 225—226°; *normal sulphate*, colourless needles ($+3H_2O$), m. p. 167—168°, or anhydrous, m. p. 172—173°; *hydrogen sulphate*, m. p. 202—203°; *normal phosphate*, brownish-yellow powder, m. p. 100°, which, when crystallised from alcohol with addition of acetone and ether, passes into the *dihydrogen phosphate*, m. p. 186°; *normal oxalate*, m. p. 123° and 202—203° (after re-solidification)]; *morphine β-chloroethyl ether*, colourless crystals, m. p. 75—76° ($+\frac{1}{2}H_2O$), 118—120° (anhydrous) [*hydrochloride*, m. p. 150—151° ($+H_2O$), 166—168° (anhydrous); *hydriodide*, yellow crystals, m. p. 212—213°; *normal sulphate*, needles, m. p. 115—120° (effervescence), and subsequently 235—240° (decomp.); *dihydrogen phosphate*, coarse crystals, m. p. about 110° (effervescence); *normal oxalate*, slender needles, m. p. 85—87°]; *morphine β-bromoethyl ether*, m. p. 135—136° (effervescence), and subsequently 185—187°, is prepared in poor yield; attempts to prepare pure *morphine ββ′-dichloroisopropyl ether* were, as expected, unsuccessful. H. W.

The Constitution of Surinamine. E. WINTERSTEIN (*Zeitsch physiol. Chem.*, 1919, **107**, 314—315. Compare A., 1919 i, 415).—The author points out the advantage of preparing surinamine by E. Fischer and W. Lipschitz's method from tyrosine
S. S. Z.

Modification of Skraup's Quinoline Synthesis. EDWARD DE BARRY BARNETT (*Chem. News*, 1920, **121**, 205—206).—By a modification of Skraup's quinoline synthesis, using the aniline and glycerol in approximately equimolecular proportions, and calcined ferric oxide instead of nitrobenzene or arsenic acid as oxidising agent, yields of 40—50% of the theoretical, calculated on both aniline and glycerol, were obtained. Increasing the proportion of glycerol did not materially improve the yield of quinoline, and it seems probable that the comparatively low yield is due more to the destruction of the aniline by the oxidising agent than to the decomposition of the glycerol, as neither the addition of boric acid nor the employment of diluted sulphuric acid or a lower temperature appreciably altered the course of the reaction. A 60% yield of quinoline was, however, obtained by mixing 50 grams of aniline, 65 grams of glycerol, and 100 grams of ferric oxide, and adding the mixture rapidly to 150 c.c. of sulphuric acid in an open dish. After keeping for half an hour, the product was worked up in the usual way. The possibility of adapting a catalytic process to the synthesis by using a small quantity of ferric oxide or stannic sulphate and oxygen gas under pressure is discussed, and indications were obtained that on a large scale the process might be successful. G. F. M.

Completely Methylated Quinic Acid. J. HERZIG and HEDWIG ORTONY (*Arch. Pharm.*, 1920, **258**, 91—96).—Exceptional difficulties have previously been encountered in methylating quinic acid; it is now found, however, that it is slowly converted into *methyl tetramethylquinate*, rhombic crystals, $a:b:c=0.6741:1:0.5960$, m. p. 56—58°, $[\alpha]_D$ $-18.5°$ in benzene solution, by repeated treatment with methyl iodide and silver oxide; the ester decomposes to some extent when distilled in a vacuum. Attempts to hydrolyse it by alkali or by aqueous hydrochloric acid did not proceed smoothly, a portion of the ester remaining unattacked whilst another portion lost the ethereal methoxy-groups to a greater or less extent. Oxidation with chromic acid in acetic acid solution or with potassium permanganate in alkaline solution, yields a mixture of unchanged ester and highly oxidised substances. It is not readily dehydrogenated by iodine. Attempts to effect methylation with methyl iodide and methyl alcohol in the presence or absence of a little copper or gold were not more successful. The action of diazomethane is rapid at first, but subsequently very slow so that the preparation of a completely methylated product in this manner is very difficult, if at all possible.

The application of Purdie's method to other cases of difficult methylation has also been investigated. 2:4:6-Trihydroxy

1 : 1 : 2 : 3 : 3 : 4 : 5 : 5 : 6-nonamethyl*cyclo*hexane (Herzig and Erthal, A., 1911, i, 778) is fairly readily converted into a monomethoxy-derivative (which could not be isolated in the pure state, owing to lack of material), but a further marked increase in the methoxy-content is not effected by eleven successive treatments of the product with methyl iodide and silver oxide. Quercitol could not be methylated under widely varied conditions.

It does not appear possible to replace the silver oxide by lead oxide. H. W.

Preparation of Diaryldialkylcarbamides. Fabriques de Produits de Chimie Organique de Laire (D.R.-P. 323534; from *Chem. Zentr.*, 1920, iv, 437—438).—The carbamyl chloride obtained from alkylated *o*-toluidine is brought into reaction with an alkylated aryl amine or alkylated *o*-toluidine, and is caused to react with the carbamyl chloride derived from another alkyl aryl amine. Thus, carbonyl chloride and ethylaniline yield *phenylethylcarbamyl chloride*, NPhEt·COCl, m. p. about 50°, which, with methyl-*o*-toluidine, gives *α-phenyl-β-o-tolyl-β-methyl-α-ethylcarbamide*, NEtPh·CO·NMe·C_6H_4Me, b. p. 180—190°/20—22 mm., 210—220°/30—32 mm., and miscible in all proportions with the common organic solvents and with collodion. Similarly, *phenylmethylcarbamyl chloride*, m. p. 88°, and ethyl-*o*-toluidine give *α-phenyl-β-o-tolyl-α-methyl-β-ethylcarbamide*,

NMePh·CO·NEt·C_6H_4Me,

b. p. 212—220°/25—27 mm. *Di-o-tolylmethylethylcarbamide*, C_6H_4Me·NEt·CO·NMe·C_6H_4Me, from *o*-tolylethylcarbamyl chloride and methyl-*o*-toluidine, has m. p. 40—42°, b. p. 205—215°/23 mm. The carbamides absorb nitrous fumes, and are expected to find application as binding agents for nitrocellulose in the preparation of explosives and celluloid. H. W.

Preparation of an Arylcarbamide. J. D. Riedel, Akt.-Ges., (D.R.-P. 323298; from *Chem. Zentr.*, 1920, iv, 437).—Ethylene chlorohydrin is allowed to react with *p*-nitrophenol, and the product, after being reduced to the corresponding amine, is transformed into the carbamide in the usual manner. *p-Nitrophenyl hydroxyethyl ether* crystallises in pale yellow needles, m. p. 94—95°. *p-Aminophenyl hydroxyethyl ether hydrochloride*, needles, m. p. 204—205°, is converted by aqueous potassium cyanate into the corresponding *carbamide*, m. p. 159—160°.

H. W.

The Action of Pyrrolidonecarboxyl Chloride on Leucine Ethyl Ester. Emil Abderhalden and Hans Spinner (*Zeitsch. physiol. Chem.*, 1919, **107**, 1—6).—The pyrrolidonecarboxyl leucine ester described by Abderhalden and Wurm (A., 1913, i, 90) is found to be a mixture. The pure ester was prepared by treating a chloroform solution of *dl*-leucine ethyl ester with *dl*-pyrrolidonecarboxyl chloride. After distilling off the chloro-

form, the syrup was extracted with absolute alcohol, and the chlorine removed by adding a calculated quantity of sodium and precipitating with alcohol. The filtrate was evaporated in a vacuum at 35—40°, and extracted with light petroleum. The residue was then dissolved in ethyl acetate. This solution, on concentration, yielded small, colourless needles, which, on purification, was found to be *glutaminyl leucine ethyl ester*, $C_{13}H_{24}O_5N_2$, m. p. 120—122°. The filtrate, on being further concentrated, yielded an orange-red syrup and oblong leaflets. The syrup was extracted with ether, and the leaflets were collected and found to be *pyrrolidonecarboxyl leucine ethyl ester*, $C_{13}H_{24}O_4N_2$, m. p. 147—148°. l-*Leucine methyl ester* was prepared by treating l-leucine ($[\alpha]_D$ +15·83°) suspended in methyl alcohol with hydrogen chloride, and then boiling for half an hour. The methyl alcohol was removed by distillation in a vacuum, and the residue dissolved in water. The aqueous solution was then extracted with ether in the presence of sodium hydroxide, and from the extract, after removal of the ether, the ester remained, b. p. 79—79·5°/12 mm., D^{17} 0·9533, $[\alpha]_D^{17}$ +16·52°. S. S. Z.

Organic Disulphides. FRITZ VON KONEK (*Ber.*, 1920, **53**, [*B*], 1666—1671).—In connexion with Lecher's recent communication on the valency problem of sulphur (this vol., i, 433), the author gives a more extended account of antipyrine and homoantipyrine (1-phenyl-3-methyl-2-ethylpyrazolone) disulphides, a short notice of which has appeared previously (A., 1911, i, 505). Although no new experimental evidence is adduced, the constitution of the compounds has become more obvious in the light of more recent research, and they are now regarded as symmetrical disulphides. The readiness with which they react with mercury when dissolved in chloroform and yield mercaptides is, however, very remarkable, particularly as Lecher has found that the various disulphides examined by him have but little tendency to dissociate into radicles, even at high temperatures. Since the disulphides of antipyrine and homoantipyrine exhibit a normal molecular weight in boiling alcohol, and therefore cannot possibly be dissociated into radicles containing univalent sulphur, the author is led to the conclusion that their smooth and quantitative transformation into mercaptides in cold chloroform solution is to be attributed to a dissociation into radicles, which only occurs under the influence of the chemical affinity of mercury for sulphur in the first moments of the action, and that this is immediately followed by union of the nascent radicles through the mercury bridge. H. W.

Action of Nitrous Fumes on Indigotin. THEODOR POSNER and GÜNTHER ASCHERMANN (*Ber.*, 1920, **53**, [*B*], 1925—1940).—Indigotin, when suspended in ethyl alcohol and treated with nitrous fumes, is gradually decolorised and dissolved, with the formation of ethyl phenylglyoxylate. In order to elucidate the probable course of the reaction, the behaviour of indigotin, when

similarly treated in the presence of a number of solvents, has been investigated, and it is thus shown that the intermediate products are derivatives, not of dehydroindigotin (compare Kalb, A., 1909, i, 966; 1910, i, 340; 1912, i, 725), but of dihydroindigotin.

Ethyl phenylglyoxylate, obtained from indigotin and nitrous fumes in the presence of ethyl alcohol (96%) at the ordinary temperature, has b. p. 138—139·2° (corr.)/12 mm., 263·6—264·6°/756 mm. (corr.; slight decomp.), and is further identified by hydrolysis to phenylglyoxylic acid, m. p. 61—63°, and conversion of the latter into its phenylhydrazone, m. p. 163°. In the presence of methyl alcohol, *methyl phenylglyoxylate*, yellow, almost odourless liquid, b. p. 136·8—137·2° (corr.)/14 mm., 254·6—255·6° (corr.)/756 mm., is produced; if the reaction is interrupted before it is complete, unchanged indigotin and isatin can also be isolated.

The action of nitrous fumes on a suspension of indigotin in ether causes the separation of *dinitrosodihydroxydihydroindigotin*,

$$C_6H_4<{}^{CO}_{N(NO)}>C(OH)\cdot C(OH)<{}^{CO}_{N(NO)}>C_6H_4,$$

yellow powder, which can be preserved for several days when perfectly pure, but, in its crude state, readily decomposes, frequently with spontaneous ignition; it becomes decomposed when slightly warmed; the mother liquors from its preparation evolve nitrous fumes and carbon monoxide violently when warmed, and yield benzoic acid. It is transformed by ethyl alcohol at 40—55° into *nitrosohydroxydihydroindigotin*,

$$C_6H_4<{}^{CO}_{NH}>CH\cdot C(OH)<{}^{CO}_{N(NO)}>C_6H_4,$$

almost colourless, crystalline powder, m. p. 194° (decomp.) after darkening at about 190°, together with small amounts of isatin. The mononitroso-compound yields an *ammonium* salt,

$C_{16}H_{11}O_4N_3,2NH_3$,

colourless powder, m. p. 168—170° (decomp. above 140°), and is transformed by uncooled methyl alcohol and nitrous fumes into *methyl phenylglyoxylate*. It is converted by boiling acetic anhydride into a mixture of *nitrosohydroxydihydroindigotin acetate*, $C_6H_4<{}^{C(OH)}_{NAc}>C\cdot C(OH)<{}^{CO}_{N(NO)}>C_6H_4$, yellow crystals, m. p. 275—278° after darkening at 265°, and *dihydroxydihydroindigotin diacetate*, $C_6H_4<{}^{C(OH)}_{NAc}>C\cdot C(OH)<{}^{CO}_{NAc}>C_6H_4$, yellow powder, m. p. above 325° after darkening at 310°, which is insoluble in all the commoner media.

Dinitrosodihydroxydihydroindigotin diacetate,

$$C_6H_4<{}^{CO}_{N(NO)}>C(OAc)\cdot C(OAc)<{}^{CO}_{N(NO)}>C_6H_4,$$

pale yellow, crystalline powder, m. p. 172° (decomp.) when rapidly heated, is prepared by the action of nitrous fumes on indigotin suspended in acetic acid; the substance cannot be pre-

served for any length of time. It is slowly converted by boiling ethyl alcohol into isatin and ethyl phenylglyoxylate, very rapidly by boiling glacial acetic acid into nitrosohydroxydihydroindigotin, m. p. 190—194° (decomp.); it is reduced by zinc dust in the presence of acetic anhydride and sodium acetate to tetra-acetyl-indigo-white, m. p. 256°.

A suspension of isatin in ethyl alcohol is gradually converted by nitrous fumes into ethyl phenylglyoxylate.

The course of the action in ethyl-alcoholic solution therefore appears to be as follows: indigotin is converted into dinitrosodihydroxydihydroindigotin, which is reduced by alcohol to nitrosohydroxydihydroindigotin on the one hand and converted into nitrosodihydroxydihydroindigotin,

$$C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C(OH)\cdot C(OH)<\begin{matrix}CO\\N(NO)\end{matrix}>C_6H_4,$$

on the other. Part of the latter is reduced to nitrosohydroxydihydroindigotin, whilst another part is oxidised to isatin and N-nitrosoisatin, $C_6H_4<\begin{matrix}CO\\N(NO)\end{matrix}>CO$. This compound unites with a molecule of alcohol, forming the diazohydrate of ethyl phenylglyoxylate, $HO\cdot N:N\cdot C_6H_4\cdot CO\cdot CO_2Et$, which is subsequently reduced by alcohol to phenylglyoxylic ester. H. W.

The Acenaphthene Series. I. The Conversion of o-Nitroamines into *iso*Oxadiazole Oxides. FREDERICK MAURICE ROWE and JOHN STANLEY HERBERT DAVIES (T., 1920, **117**, 1344—1351).

The Sulphonation of Glyoxalines. FRANK LEE PYMAN and LEONARD ALLAN RAVALD (T., 1920, **117**, 1429—1431).

The Formation and Reactions of Imino-compounds. XX. The Condensation of Aldehydes with Cyanoacetamide. JAMES NELSON EDMUND DAY and JOCELYN FIELD THORPE (T., 1920, **117**, 1465—1474).

Iminazole*iso*piperidine [Tetrahydro-1 : 3 : 5-benztriazole] and its Derivatives. SIGMUND FRÄNKEL and KAROLINE ZEIMER (*Biochem. Zeitsch.*, 1920, **110**, 234—244).—4-β-Aminoethylglyoxaline was prepared by eliminating the carboxyl group of histidine hydrochloride by means of bacterial action. It was then treated with concentrated hydrochloric acid and methylal on the water-bath under a reflux condenser. The product of the reaction was freed from the hydrochloric acid by evaporation, and recrystallised from alcohol. The tetrahydro-1:3:5-benztriazole hydrochloride thus obtained forms triclinic crystals, m. p. 253°. *Tetrahydro-1:3:5-benztriazole*, $CH<\begin{matrix}NH\cdot C\cdot CH_2\cdot CH_2\\N=C\cdot CH_2\cdot NH\end{matrix}$, obtained by treating the hydro-

[illegible]

following derivatives were prepared: *dipicrate*,

$$C_6H_9N_3(C_6H_3O_7N_3)_2,$$

m. p. 220°; *dipicrolonate*, $C_6H_9N_3(C_{10}H_8O_5N_4)_2$,EtOH, m. p. 250°; *aurichloride*, $C_6H_9N_3$,$AuCl_3$, m. p. 217°; *platinichloride*,

$$C_6H_9N_3PtCl_6,H_2O,$$

decomp. 280°; *mercurichloride*, $C_6H_9N_3(HgCl_2)_4$, m. p. 210°; N-*acetyl-hydrochloride*, $C_6H_8N_3Ac$,HCl,H_2O, m. p. 235°; N-*dibenzoyl* derivative, $C_6H_7N_3Bz_2$,H_2O, m. p. 215°. Hydroxyhydro*iso*quinoline was prepared by treating tyramine with concentrated hydrochloric acid and methylal on the water-bath under the reflux condenser. S. S. Z.

Uroxanic Acid. HEINRICH BILTZ and RUDOLF ROBL (*Ber.*, 1920, **53**, [*B*], 1950—1963).—Uroxanic acid has been largely investigated by Behrend (A., 1904, i, 950) and Behrend and Schultz (A., 1909, i, 272), and it has been shown that, in all probability, the substance is dicarbamidomalonic acid,

$$(NH_2\cdot CO\cdot NH)_2C(CO_2H)_2.$$

This view of its constitution has now been fully confirmed.

Potassium uroxanate is moderately rapidly obtained by the oxidation of a solution of uric acid in an excess of aqueous potassium hydroxide by purified air at 38°, and very slowly prepared in a similar manner at the ordinary temperature; the oxidation is, however, more conveniently effected with aqueous potassium permanganate, the yield being 27% of that theoretically possible (allantoin is also formed). The salt forms colourless crystals, $a:b:c=0.88576:1:1.2044$, and gives hydrates containing 3·5, 3, and probably also 0·5 H_2O. Uroxanic acid crystallises in indistinct tetrahedra, decomp. 162° [the sodium salt, hexagonal leaflets ($+8H_2O$), anhydrous *ammonium* salt, prisms, decomp. 182° after becoming discoloured at about 172°, and the *silver* salt, colourless, crystalline powder, are described]. Uroxanic acid is reduced by fuming hydriodic acid to hydantoin, and, hydrolysed by warm water (with loss of carbon dioxide), to carbamide and "glyoxylcarbamide," decomp. 120—125° (compare following abstract), the latter change being also effected by concentrated nitric acid. Cold dilute hydrochloric acid transforms it into allantoin, whilst *spiro*-dihydantoin (A., 1917, i, 290) is formed under similar conditions with concentrated hydrochloric acid.

Esterification of the carboxy-groups of uroxanic acid cannot be effected with methyl alcohol and hydrogen chloride, with methyl sulphate in alkaline solution, or from the silver salt and methyl iodide; with the aid of diazomethane, however, it has been found possible to prepare *methyl uroxanate*, decomp. 213°, which is slowly hydrolysed to uroxanic acid by aqueous potassium hydroxide solution, and converted by boiling water into *spiro*-*dihydantoin*, which is conveniently identified as the di-silver salt, $C_5H_2O_4N_4Ag_2$,$2H_2O$, and the *diammine copper* salt,

$$C_5H_2O_4N_4[Cu(NH_3)_2],$$

pale blue, matted needles.

The presence of the two carbamido-groups is deduced from the behaviour of the substance towards nitrous acid, which, under definite conditions (see later), leads to the quantitative evolution of the whole of the nitrogen. It is shown at the instance of uric acid, uric acid glycol, methyl urate, hydantoin, glyoxylcarbamide, and alloxanic acid that nitrogen united in a ring is not liberated by nitrous acid in these circumstances, whilst, on the other hand, the nitrogen of primary amines and of substances which contain the carbamido-group as an open chain, and in which an alkyl group is not attached to the nitrogen atom, is evolved in the free state. Whilst the former statement appears to be universally true, the latter is subject to certain exceptions, since, although it is valid in the cases of methylamine hydrochloride, glycine, leucine, carbamide, *as*-dimethylcarbamide, allantoic acid, and 1:3:7-trimethyl-ψ-uric acid, it does not hold for certain methylated allantoins in which the expected decomposition does not occur, nor for derivatives of carbamide containing negative substituents (acetylcarbamide, benzoylcarbamide, allophanic ester, ψ-uric acid, 5-methoxy-ψ-uric acid), which are not decomposed. For the estimation of the nitrogen, a weighed quantity of the substance is placed with about 1 gram of solid sodium nitrite in a flask through which a current of carbon dioxide can be passed, and provided with a dropping funnel, and connected through bulbs containing a solution of chromium trioxide (100 grams) in nitric acid (12%; 100 c.c.) to a nitrometer filled with potassium hydroxide solution. The apparatus is filled with carbon dioxide, and sodium nitrite solution (40%; 20 c.c.) is admitted, followed by 2*N*-sulphuric acid, the rate of addition of the latter being so controlled that the solution retains a green colour and evolves oxides of nitrogen. After completion of the action, the residual nitrogen is driven into the nitrometer by carbon dioxide.

Elimination of the carbamido-groups from uroxanic acid by means of sodium nitrite leads to the formation of mesoxalic acid.

H. W.

Mechanism of the Formation of Uroxanic Acid from Uric Acid. HEINRICH BILTZ and FRITZ MAX (*Ber.*, 1920, **53**, [*B*], 1964—1966).—It can scarcely be doubted that the primary product of the oxidation of uric acid in alkaline solutions contains two hydroxyl groups in the 4:5-positions, but all attempts to prepare uroxanic acid directly from the uric acid-4:5-glycol have failed. It is now shown, however, that it can be obtained when the corresponding dimethyl ether is gently warmed with dilute alkali. It is therefore quite possible that the formation of the glycol is the first step in the conversion of uric into uroxanic acid, but that the spatial configuration of the intermediate glycol differs from that of the isolated compound. The further action probably proceeds either through *spiro*dihydantoin or hydroxydicarbamidoethanecarboxylic ester, $CO<\begin{matrix}NH\cdot C(CO_2R)\cdot NH\\NH\cdot C(OH)—NH\end{matrix}>CO$; the former has been shown to be convertible into uroxanic acid (Biltz and Heyn, *A.*,

1917, i, 290), but, for other reasons, the authors consider the latter to be the more probable intermediate substance. H. W.

Oxonic Acid. Heinrich Biltz and Rudolf Robl (*Ber.*, 1920, **53**, [*B*], 1967—1983).—Oxonic acid in the form of its potassium, potassium hydrogen, sodium, ammonium hydrogen, and barium hydrogen salts was isolated by Strecker from the products of the slow oxidation of alkaline solutions of uric acid by air, and the account of the work was published after Strecker's death by Medicus (this Journ., 1875, 555). Since then, very little progress has been made with the investigation of the substance, largely owing to its difficult accessibility. The present authors find that potassium hydrogen oxonate can be rapidly prepared by addition of finely divided potassium permanganate to a solution of uric acid in an excess of aqueous potassium hydroxide at 30—40°, followed by cautious addition of acetic acid. The identity of the oxonic acid derivatives obtained in this manner with Strecker's preparation is established by comparison of a series of salts. A further advance is made through the observation that free *oxonic acid*, platelets ($+2H_2O$), can be obtained by the action of hydrochloric acid (10%) on the potassium hydrogen salt; as is to be expected, it is very unstable, and evolves carbon dioxide when treated with water at 40°, passing thereby into a substance, which Strecker merely designates "new acid from oxonic acid," but Medicus (*loc. cit.*) describes as "crystalline glyoxylurea," $CO<\begin{matrix}NH\cdot CH\cdot OH\\NH\cdot CO\end{matrix}$. Complete analyses of this substance have shown that this formula is incorrect, and that it actually has the composition $C_3H_3O_3N_3$, and is identical with allantoxaidin, which has been prepared by Mulder (A., 1871, 1197) and van Embden (this Journ., 1873, 1025) by the oxidation of allantoïn by potassium ferricyanide in alkaline solution, and the constitution of which has been elucidated by Ponomarew (A., 1879, 226). Oxonic acid is therefore identical with allantoxanic acid, $CO<\begin{matrix}NH\cdot C{:}N\cdot CO_2H\\NH\cdot CO\end{matrix}$. Its production from uric acid is explained according to the scheme: uric acid →

$$CO<\begin{matrix}NH\cdot C(CO_2H)\cdot NH\\NH\cdot C(OH)—NH\end{matrix}>CO \rightarrow CO<\begin{matrix}NH\cdot C=\!=\!=\!=N\\NH\cdot C(OH)\cdot NH\end{matrix}>CO \rightarrow$$

$$CO<\begin{matrix}NH\cdot C{:}N\cdot CO\cdot NH_2\\NH\cdot CO\end{matrix} \rightarrow CO<\begin{matrix}NH\cdot C{:}N\cdot CO_2H\\NH\cdot CO\end{matrix}.$$

The work described in this and the preceding abstracts allows a fairly complete picture to be drawn of the oxidation of uric acid in alkaline solution. If the latter is concentrated and cooled, potassium uroxonate separates; if it is acidified with acetic acid (particularly after addition of alcohol), potassium hydrogen oxonate crystallises, whilst if the acidified solution is preserved or evaporated and cooled, allantoin is obtained.

The following substances are described: *methyl oxonate*, viscous

syrup, which could not be caused to crystallise; *normal potassium oxonate*, $C_4HO_4N_3K_2,H_2O$; *zinc hydrogen oxonate*, thin platelets ($+4H_2O$); normal lead oxonate, small, rhombic crystals; normal silver oxonate, voluminous precipitate; the silver salt, dense, white precipitate; *hydrazine* salt, slender needles, m. p. 204°, and *phenylhydrazine* salt, pale yellow leaflets, m. p. 228° (decomp.), of allantoxaidin.

A solution of oxonic acid is almost quantitatively oxidised to cyanuric acid by potassium permanganate in the presence of sulphuric acid.

Dehydrated allantoxaidin is converted by an ethereal solution of diazomethane into *dimethylallantoxaidin*, short prisms, m. p. 158°; the same compound is obtained from the silver salt of allantoxaidin and methyl iodide. Both methyl groups are attached to nitrogen. Dilute mineral acids decompose allantoxaidin into formic acid and biuret; concentrated nitric acid causes a similar decomposition, yielding, however, 1-*nitrobiuret*, decomp. 165°.

Ponomarew's synthetic production of oxonic acid (allantoxanic acid) from parabanic acid and carbamide is confirmed; similarly, methylparabanic acid and carbamide give an amorphous, yellow condensation *product*, decomp. ca. 200°, which is converted by potassium hydroxide into a crystalline *potassium* salt, yielding (?) *methyloxonic acid*, decomp. 135°. On the other hand, dimethylparabanic acid could not be condensed with carbamide, methylcarbamide, or *s*- or *as*-dimethylcarbamide. H. W.

Pyrrole-blacks. VIII. A. Angeli and C. Lutri (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 420—423. Compare this vol., i, 397).—A black substance identical in composition and properties with that obtained by the interaction of pyrrole and *p*-benzoquinone in presence of water is formed when this reaction takes place in acetic acid solution. It is therefore probable that this substance represents an individual compound, and it is assumed that, in its formation, the quinonoid and pyrrole rings unite.

When treated with nitrous acid, pyrrole yields intensely black products (compare Angeli and Cusmano, A., 1917, i, 413), and it is now found that the interaction of pyrrole and *p*-nitrosophenol in cold acetic acid gives an amorphous, deep violet-black powder insoluble in the ordinary solvents, but soluble in alkalis, giving black solutions; this powder has a composition corresponding with the formula $C_{32}H_{22}O_5N_6$ or $C_{32}H_{24}O_5N_6$, and appears to be formed according to one of the two equations:

$$2C_4H_5N + 4C_6H_5O_2N - 3H_2O - H_2 = C_{32}O_{22}O_5N_6$$

or $2C_4H_5N + 4C_6H_5O_2N - 3H_2O = C_{32}H_{24}O_5N_6$.

Intensely coloured products are formed also by the action of pyrrole on *p*-quinoneimine or *p*-quinonedi-imine. T. H. P.

Catalytic Reduction of *o*-Nitroazoxybenzene. Guido Cusmano (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 93—95).—When an ethereal solution of *mm'*-dinitroazoxybenzene, contain-

ing platinum-black in suspension, is shaken at the ordinary temperature in an atmosphere of hydrogen, the gas is rapidly absorbed, with formation of various reduction products, principally *o-aminoazoxybenzene*, $NH_2 \cdot C_6H_4 \cdot N:NPh:O$, which crystallises in long, flattened prisms, m. p. 97°, forms colourless, well-crystallised salts with hydrochloric and sulphuric acids, and yields an *acetyl* derivative, m. p. 157°. When heated on a boiling-water bath with concentrated sulphuric acid, it does not undergo Wallach's transposition, according to which azoxybenzenes are converted into the isomeric hydroxyazo-compounds, but it suffers intramolecular dehydration, with formation of 2-phenyl-1:2:3-benztriazole, $C_6H_4 < \overset{N}{\underset{N}{|}} > NPh$ or $C_6H_4 \lessdot \overset{N}{\underset{N}{}} > NPh$. The detailed results are to be published later. T. H. P.

Electrolytic Reduction of Hydroxyazo-compounds. II. E. PUXEDDU (*Gazzetta*, 1920, **50**, ii, 149—159. Compare A., 1918, i, 551).—Further experiments on the electrolytic reduction of hydroxyazo-compounds, mostly in acid solution, show that such reduction always consists in rupture of the azo-linking, with formation of two bases, namely, the aniline used to prepare the hydroxyazo-compound and the aminophenol, corresponding with the phenol used in this preparation; no other reduction products have been isolated.

In presence of sodium hydroxide, the electrolytic reduction of *p*-benzeneazophenol proceeds with difficulty, and gives poor yields. In acid solution, 3-benzeneazo-*o*-cresol yields aniline and 5-amino-*o*-cresol, but in alkaline solution only the aniline is detectable. Other compounds investigated were 4-*o*-tolueneazophenol and 4-*p*-tolueneazophenol. T. H. P.

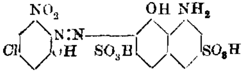
Diazotisation of Polynitroanilines. EMIL MISSLIN (*Helv. Chim. Acta*, 1920, **3**, 626—639).—The loosening influence which the diazo-group exerts on ortho-substituents is enhanced, especially by negative groups in the para-position, and this becomes of importance if the behaviour of more highly negatively substituted dinitroanilines on diazotisation is to be studied. Up to the present, picramide has been regarded as incapable of diazotisation, as it does not yield to the methods usually employed to meet such cases. Even with 4-chloro-2:6-dinitroaniline, it is easily seen that the diazonium compound, obtained by treatment of its concentrated sulphuric acid solution with nitrosylsulphuric acid in the cold, loses increasing amounts of nitrous acid after being poured into ice-water and allowed to remain, the power of coupling with β-naphthol also diminishing; it is found that one of the nitro-groups undergoes replacement by hydroxyl.

Similar, but still more pronounced, behaviour is shown by a diazotised solution of 2:6-dinitroaniline-4-sulphonic acid in concentrated mineral acid; this is stable, but, on neutralisation with sodium acetate or sodium hydrogen carbonate, an ortho-nitro-group is eliminated and replaced by hydroxyl.

As regards the properties which must be shown by diazotised 2:4:6-trinitroaniline solutions, Witt's assumption that amines such as this, which are unable to form salts, are absolutely undiazotisable (A., 1909, i, 855), is beside the mark, since the solution of this amine in concentrated sulphuric acid undoubtedly contains picramide sulphate. There is hence no ground for assuming that picramide cannot be diazotised, the only necessary condition being the exclusion during the process of diazotisation of the hydrolysing action of water, which is indirectly the cause of the loosening influence of the diazo-group.

On these considerations is based the following method for diazotising di- and tri-nitroanilines of the type of picramide. The amine is dissolved in glacial acetic acid and the solution treated carefully in the cold with nitrosylsulphuric acid or with a solution of sodium nitrite in sulphuric acid monohydrate, the weight of the latter used in the case of trinitroanilines being equal to that of the acetic acid used for dissolving the amine. If much less sulphuric acid is taken, say 2 mols. per 1 mol. of amine, no diazotisation takes place, even in glacial acetic acid, excess of sulphuric or nitrosylsulphuric acid being evidently necessary to give the sulphate of the amine. By this method, 2:4:6-trinitroaniline, 2:4:6-trinitro-3-methoxyaniline, 2:4:6-trinitro-3-ethoxyaniline, and 2:4:6-trinitro-3-hydroxyaniline have been diazotised and coupled with β-naphthol to form colouring matters, the yield of the latter in the pure state amounting to 80%. Further, 2:4:6-trinitro-*m*-phenylenediamine has been tetrazotised by this method, but the diazotisability of 2:3:4:6-tetranitroaniline remains uncertain.

Diazotisation of 4-*chloro*-2:6-*dinitroaniline, and coupling of the product* with 1:8-aminonaphthol-3:6-disulphonic acid, yields the *colouring matter* (annexed formula), which crystallises in small, bronzed needles and exhibits the properties of a typical *o*-hydroxyazo-colouring matter; in a faintly acid bath, it dyes wool bluish-Bordeaux, the *colour being sensitive to acid,* and yielding pure blue and violet-black tints when treated with copper sulphate and chromed respectively. With β-naphthol, the diazo-solution forms the *colouring matter*, $C_{16}H_9O_5N_4Cl$, which separates in stout, reddish-brown, shining crystals, dissolves in concentrated sulphuric acid to a violet-blue solution, and is precipitated from the latter unaltered by addition of water. Freshly prepared 4-chloro-2:6-dinitroaniline diazo-solution gives, with a solution of β-naphthol-6-sulphonic acid rendered alkaline with sodium carbonate, a colouring matter which colours wool yellowish-orange, and with 1:8-aminonaphthol-3:6-disulphonic acid in alkaline solution, a monoazo-colouring matter, which dyes wool bluish-Bordeaux, and in which the two nitro-groups in the ortho-positions to the amino-group still persist. The *colouring matter* formed by



coupling with α-naphthol crystallises in slender, brownish-yellow, shining needles ($+1C_2H_4O_2$), dissolves in concentrated sulphuric acid to a violet-blue solution, and is precipitated unchanged from the latter by addition of water. Typical for the α-naphthol colouring matter is the property of dissolving in dilute sodium hydroxide solution to a deep blue solution, from which sodium or potassium chloride precipitates the corresponding salt in shining crystals resembling crystal-violet. This behaviour confirms the expectation that the union with α-naphthol takes place in the para-position to the hydroxyl group; the β-naphtholazo-colouring matter is insoluble in cold aqueous sodium hydroxide. Noteworthy is the great affinity towards wool of the α-naphthol product in dilute sodium hydroxide. The deep blue coloration is converted into orange by atmospheric carbon dioxide.

Diazotised 2:6-dinitroaniline-4-sulphonic acid gives with β-naphthol a typical *o-hydroxy-colouring matter*,

$$C_{16}H_{10}O_8N_4S,2H_2O,$$

which forms shining, brownish-orange needles, and in faintly acid bath colours wool bright orange; the coloration is sensitive to alkali, and is turned blue by ammonia, the colouring matter being destroyed by boiling with dilute sodium hydroxide. The corresponding *α-naphtholazo-colouring matter* forms a brownish-yellow, crystalline powder, and in faintly acid solution produces on wool yellowish-brown tints, which are still more sensitive to alkali, being changed to deep blue, even by dilute sodium carbonate solution.

Diazotisation of picramide and coupling with β-naphthol yields the *colouring matter*, $C_{16}H_9O_7N_5$, which crystallises in greenish-blue, spear-like crystals with metallic lustre, or in shining, reddish-brown cubes; it dissolves in concentrated sulphuric acid, giving a blue solution. The corresponding α-naphthol *compound* forms shining, yellowish-brown crystals, giving a violet-blue solution in concentrated sulphuric acid.

Diazotisation of 2:4:6-trinitro-3-hydroxyaniline and coupling with β-naphthol gives the *colouring matter*, which separates in brownish-black crystals with metallic lustre, and yields a blue solution in concentrated sulphuric acid and a Bordeaux solution in dilute sodium hydroxide solution; gentle heating of the alkaline solution destroys the colouring matter. 2:4:6-Trinitro-3-methoxy- (and ethoxy-) anilines yield similar compounds, and 2:4:6-trinitro-*m*-phenylenediamine the corresponding tetrazo-colouring matter.

T. H. P.

Action of Diazonium Salts on Arylsulphonated Aceto- and Propio-nitriles. J. Tröger and E. Wunderlich (*J. pr. Chem.*, 1920, [ii], **101**, 157—170. Compare A., 1905, i, 336, 870; 1908, i, 798; 1915, i, 792).—Arylsulphonated acetonitriles have been shown to differ in behaviour from arylsulphonated propionitriles, since they readily dissolve in alkali hydroxide solution, in which the latter are insoluble. Both classes of compounds are now shown to react with diazonium salts. The propionitrile

derivatives so obtained must necessarily be regarded as azo-compounds, but the acetonitrile derivatives may be either azo-compounds, $R\cdot SO_2\cdot CH(\cdot N:NR)\cdot CN$, or hydrazones,

$$R\cdot SO_2\cdot C(:N\cdot NHR)\cdot CN;$$

the latter assumption is the more probable, since the derivatives, like the parent substance, are soluble in alkali hydroxide solution. Attempts to adduce more definite evidence did not meet with success. Assuming the acetonitrile compound to be a true azo-derivative, it should pass, when methylated, into the corresponding propionyl compound; this does not appear to be the case, but the processes of methylation and purification of the methylated product are beset by unusual difficulties, so that trustworthy conclusions can scarcely be drawn. An attempt to prepare an undoubted hydrazone of an acetonitrile compound was made at the instance of α-naphthalenesulphonyldibromoacetonitrile,

$$C_{10}H_7\cdot SO_2\cdot CBr_2\cdot CN,$$

which, however, could not be induced to react with phenylhydrazine in the desired sense, the ultimate product being α-naphthalenesulphonylacetonitrile.

The compounds are prepared either by the addition of the diazonium solution to a well-cooled solution of the nitrile in an excess of aqueous sodium hydroxide, followed by acidification with acetic acid, or by slowly running the diazonium solution into an alcoholic solution of the nitrile in the presence of saturated aqueous sodium acetate solution; only the second process is available in the case of the propionitrile derivatives.

The following compounds have been prepared: α-naphthalenesulphonylacetonitrile, m. p. 111—112° (Tröger and Helle, *loc. cit.*, give 109°); *α-naphthalenesulphonylbenzeneazoacetonitrile* or *phenylhydrazone* of *α-naphthalenesulphonylformyl cyanide*, reddish-yellow, six-sided crystals, m. p. 203° [*potassium* salt ($+3H_2O$), golden-yellow crystals; *sodium* salt, freely soluble in water, and not obtained in the crystalline state; *lead* salt, canary-yellow, amorphous precipitate; *silver* salt, canary-yellow precipitate]; *α-naphthalenesulphonyl*-p-*tolueneazoacetonitrile* or p-*tolylhydrazone* of *α-naphthalenesulphonylformyl cyanide*, orange-red leaflets, m. p. 193° [*potassium* salt, golden-yellow, shining crystals ($+3H_2O$); *silver* salt, dark yellow, amorphous precipitate; *sodium* salt, freely soluble in water]; *α-naphthalenesulphonyl*-o-*tolueneazoacetonitrile* or o-*tolylhydrazone* of *α-naphthalenesulphonylformyl cyanide*, dark yellow, prismatic needles, m. p. 149—150° (*potassium* salt, pale yellow needles; *sodium* salt, freely soluble in water); *α-naphthalenesulphonyl*-p-*anisoleazoacetonitrile* or p-*methoxyphenylhydrazone* of *α-naphthalenesulphonylformyl cyanide*, carmine-red, prismatic needles, m. p. 173° [*potassium* salt, pale yellow, six-sided crystals ($+H_2O$); *sodium* salt, freely soluble in water]; *β-naphthalenesulphonylbenzeneazoacetonitrile* or *phenylhydrazone* of *β-naphthalenesulphonylformyl cyanide*, red needles, m. p. 194—195° [*potassium* salt ($+3H_2O$), yellowish-brown, shining crystals; *sodium* salt, freely soluble in water; *lead* salt, lemon-yellow,

amorphous precipitate]; β-naphthalenesulphonylacetonitrile has m. p. 109° (instead of 95°, as previously given); methylation of the substance, m. p. 194—195°, by *methyl iodide* and *sodium* ethoxide at 100° gives a product, yellowish-red crystals, m. p. 168°, which differs from the corresponding propionyl compound (see later), but other analogous experiments failed to give so definite a result; *β-naphthalenesulphonyl*-p-*tolueneazoacetonitrile* or p-*tolylhydrazone* of *β-naphthalenesulphonylformyl cyanide*, orange-coloured needles, m. p. 189—190° [*potassium* salt ($+0.5H_2O$), amorphous, egg-yellow substance; *sodium* salt, freely soluble in water; *silver* salt, amorphous, dark yellow precipitate]; *methylated product*, pale yellow needles, m. p. 210—211°; *β-naphthalenesulphonyl*-m-*tolueneazoacetonitrile* or m-*tolylhydrazone* of *β-naphthalenesulphonylformyl cyanide*, red, prismatic needles, m. p. 160—161° (*potassium* salt, reddish-yellow crystals; *sodium* salt, freely soluble in water); *β-naphthalenesulphonyl*-p-*phenetoleazoacetonitrile* or p-*ethoxyphenylhydrazone* of *β-naphthalenesulphonylformyl cyanide*, pale brown crystals, m. p. 165—166° [*potassium* salt ($+3H_2O$), dark yellow, hexagonal crystals]; p-*bromobenzenesulphonylbenzeneazoacetonitrile* or *phenylhydrazone* of p-*bromobenzenesulphonylformyl cyanide*, yellowish-brown prisms, m. p. 185° (*sodium* salt, pale yellow, amorphous precipitate); p-*bromobenzenesulphonyl*-p-*phenetoleazoacetonitrile* or p-*ethoxyphenylhydrazone* of p-*bromobenzenesulphonylformyl cyanide*, pale brown, prismatic needles, m. p. 154—155° (*sodium* salt, dark yellow crystals) (in the two cases last mentioned, the salts can only be prepared in the absence of moisture); *benzenesulphonylbenzeneazopropionitrile*, $SO_2Ph\cdot CMe(N_2Ph)\cdot CN$, canary-yellow, prismatic needles, m. p. 78°; *benzenesulphonyl*-p-*tolueneazopropionitrile*, red, prismatic needles, m. p. 103—104°; *benzenesulphonyl*-p-*anisoleazopropionitrile*, lemon-yellow needles, m. p. 81—82°; *benzenesulphonyl*-p-*phenetoleazopropionitrile*, pale yellow crystals, m. p. 96—97°; *β-naphthalenesulphonylpropionitrile*, colourless, waxy crystals, m. p. 90—91°; *β-naphthalenesulphonylbenzeneazopropionitrile*, dark yellow tetrahedra, m. p. 120°; *β-naphthalenesulphonyl*-p-*tolueneazopropionitrile*, dark yellow prisms, m. p. 119—120°; p-*chlorobenzenesulphonylbenzeneazopropionitrile*, dark yellow rhombs, m. p. 90—91°; p-*chlorobenzenesulphonyl-β-naphthaleneazopropionitrile*, pale yellow, silky needles, m. p. 154—155°; p-*bromobenzenesulphonyl*-p-*tolueneazopropionitrile*, dark yellow, prismatic needles, m. p. 151°; p-*bromobenzenesulphonyl*-p-*anisolepropionitrile*, sulphur-yellow prisms, m. p. 153°. H. W.

o-, *m*-, and *p*-**Tolueneazo-α-naphthylhydrazinesulphonic Acids.** J. Tröger and G. Lange (*J. pr. Chem.*, 1920, [ii], **101**, 123—135. Compare A., 1906, i, 120; 1909, i, 68, 69; 1910, i, 207).—The *o*-, *m*-, and *p*-tolueneazo-α-naphthylamines are diazotised, and the resulting solutions are filtered into alkaline potassium sulphite solution, thus yielding the potassium diazo-

sulphonates, $C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot SO_3K$; the latter are reduced by ammonium sulphide to the corresponding potassium hydrazine sulphonates, $C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot NH\cdot NH\cdot SO_3K$ (which are somewhat readily decomposed), from which the free sulphonic acids are readily isolated. The yields are dependent on the smoothness with which the primary material can be diazotised; with the ortho- and meta-derivatives, this occurs readily at 0°, but with the para-compound it is best effected at 20°, the process, however, being rather unsatisfactory even in this case. The hydrazinesulphonic acid reacts with aromatic aldehydes to yield hydrazones; heating during the reaction must not be prolonged, and the meta- and para-compounds are more sensitive than the ortho-derivatives.

The following substances are described: *potassium* p-*tolueneazo-α-naphthyldiazosulphonate* (labile salt, amorphous, reddish-brown flocks; stable salt, dark brown powder); *potassium* p-*tolueneazo-α-naphthylhydrazinesulphonate*, pale brown needles; p-*tolueneazo-α-naphthylhydrazinesulphonic acid*, blackish-violet crystals; p-*tolueneazo-α-naphthyl-o-hydroxybenzylidenehydrazine*,

$$C_6H_4Me\cdot N{:}N\cdot C_{10}H_6\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OH,$$

dark reddish-brown, prismatic needles, m. p. 166·5° (*hydrochloride*, dark moss-green, crystalline powder); p-*tolueneazo-α-naphthylcinnamylidenehydrazine*, dark reddish-brown, prismatic crystals, m. p. 168·5° after previous softening (*hydrochloride*, black powder with green glance); p-*tolueneazo-α-naphthylanisylidenehydrazine*, small, brown, shining crystals, m. p. 156° (*hydrochloride*, blackish-green crystals); *tolueneazo-α-naphthyl*-p-*tolylidenehydrazine*, blackish-brown, oblique crystals, m. p. 159° (*hydrochloride*, small, bluish-black crystals).

o-*Tolueneazo-α-naphthylamine*, pale red, silky needles, m. p. 99° [the *hydrochloride*, violet needles, *sulphate*, pale violet crystals ($+3H_2O$), and the *nitrate*, blackish-green crystals, are described], is most conveniently prepared by the addition of diazotised *o*-toluidine solution to an alcoholic solution of α-naphthylamine at 45°. It gives rise to the following compounds: *potassium* o-*tolueneazo-α-naphthyldiazosulphonate* (red, labile, and rust-red stable salt); *potassium* o-*tolueneazo-α-naphthylhydrazinesulphonate*, pale brown, silky leaflets; o-*tolueneazo-α-naphthylhydrazinesulphonic acid*, amorphous, violet-black flocks; o-*tolueneazo-α-naphthyl-o-hydroxybenzylidenehydrazine*, coarse, dark brown crystals, m. p. 162° (*hydrochloride*, bluish-green, crystalline powder); o-*tolueneazo-α-naphthylcinnamylidenehydrazine*, brown prisms, m. p. 170° (*hydrochloride*, coarse, black, crystalline powder); o-*tolueneazo-α-naphthylanisylidenehydrazine*, brown, shining leaflets, m. p. 153° (*hydrochloride*, small, dark blue crystals); o-*tolueneazo-α-naphthyl*-p-*tolylidenehydrazine*, coffee-brown crystals, m. p. 152° (*hydrochloride*, black, shining, crystalline powder).

m-*Tolueneazo-α-naphthylamine*, blood-red crystals, m. p. 107° [*nitrate*, bluish-violet needles; *chloride* ($+2H_2O$), black, silky needles; *sulphate*, steel-blue rods], yields *potassium* m-*tolueneazo-*

α-naphthylhydrazinesulphonate, small, reddish-brown needles, and *m-tolueneazo-α-naphthylhydrazinesulphonic acid*, violet crystals. The latter reacts with anisaldehyde to give *m-tolueneazo-α-naphthylanisylidenehydrazine*, small, coffee-brown crystals, m. p. 159—160° (*hydrochloride*, bluish-black, crystalline powder).

H. W.

o- and p-Tolueneazoglyoxalines. FRANK LEE PYMAN and LEONARD ALLAN RAVALD (T., 1920, **117**, 1426—1429).

Nitro-derivatives and Nitrohydrazones. II. R. CIUSA and L. VECCHIOTTI (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 42—47. Compare A., 1912, i, 133; this vol., i, 256).—The tendency of the phenylhydrazones of aromatic nitro-aldehydes to furnish chromo-isomerides is exhibited to an enhanced degree by the nitrophenylhydrazones. As regards the cause of this isomerism, it has been found previously (A., 1912, i, 33) that, whereas benzaldehydephenylhydrazone (1 mol.) forms an additive compound with 2 mols. of picryl chloride, each of the phenylhydrazones of the three nitrobenzaldehydes unites with only 1 mol. of the chloride, although benzaldehydenitrophenylhydrazone unites with 2 mols. The conclusion is drawn that the points of attack in the molecules of trinitrobenzene and its derivatives are the phenyl group of the aldehyde and the iminic nitrogen atom. In order to test this conclusion, additive componnds of benzaldehydephenylhydrazone with two different trinitrobenzene derivatives have been prepared with the hope of obtaining two such isomerides as

$C_6H_2Cl(NO_2)_3 \cdots CHPh{:}N{\cdot}NHPh \cdots C_6H_2Me(NO_2)_3$

and $C_6H_2Me(NO_2)_3 \cdots CHPh{:}N{\cdot}NHPh \cdots C_6H_2Cl(NO_2)_3$; as yet, no such isomerides have been obtained.

The possibility that, in the chromo-isomeric nitrophenylhydrazones, the nitro-group is united internally by secondary valencies either to the iminic nitrogen atom or to the phenyl group of the aldehyde, is also discussed.

The experimental results obtained are to be published separately.

T. H. P.

The Influence of Reaction on the Precipitation of Protein by Tannin. TORALD SOLLMANN (*J. Pharm. expt. Ther.*, 1920, **16**, 49—59).—The precipitation of proteins by tannin depends on the hydrogen-ion concentration of the medium. The application of these observations to the clinical nse of astringents is discussed.

J. C. D.

The Balloelectricity of Amphoteric Substances. C. CHRISTIANSEN and JOHANNE CHRISTIANSEN (*Zeitsch. physiol. Chem.*, 1919, **107**, 7—28).—The isoelectric point of certain substances, such as albumin, leucine, etc., is identical with the isoballoelectric point. Other ampholytes, such as glycine, alanine, etc., show no isoballoelectric point. The authors presume that

this differentiation in balloelectric behaviour of ampholyte ions is connected with the hydration of the ions. S. S. Z.

Ion Series and the Physical Properties of Proteins. I. JACQUES LOEB (*J. Gen. Physiol.*, 1920, **3**, 85—105).—Experiments are described on the influence of acids and alkalis on the osmotic pressure of solutions of crystalline egg-albumin and of gelatin, and on the viscosity of solutions of gelatin. It was found that in all cases there was no difference in the effects of hydrochloric, hydrobromic, nitric, acetic, mono-, di-, and tri-chloroacetic, succinic, tartaric, citric, and phosphoric acids on these physical properties when the solutions of the protein with these different acids have the same hydrogen-ion concentration and the same concentration of originally isoelectric protein. It was possible to show that in all the protein acid salts named, the anion in combination with the protein is univalent.

The strong bibasic sulphuric acid forms protein acid salts with a bivalent anion, SO_4, and the solutions of protein sulphate have an osmotic pressure and a viscosity of only half or less than that of a protein chloride solution of the same concentration of hydrogen ions and originally isoelectric protein. Oxalic acid behaves essentially like a weak bibasic acid, although it seems that a small part of the acid combines with the protein in the form of bivalent anions. It was found that the osmotic pressure and viscosity of solutions of lithium, sodium, potassium, and ammonium salts of a protein are the same at the same hydrogen-ion concentration and the same concentration of originally isoelectric protein. Calcium and barium hydroxides form salts in which the cation is bivalent, and the osmotic pressures and viscosity of solutions of these two metal proteinates are only one-half or less than half of that of sodium proteinate of the same concentrations of hydrogen ion and originally isoelectric protein.

These results exclude the possibility of expressing the effect of acids and alkalis on the osmotic pressure of solutions of gelatin and egg-albumin, and on the viscosity of solutions of gelatin in the form of ion series. The different results of former workers were probably chiefly due to the fact that the effects of acids and alkalis on these proteins were compared for the same quantity of acid and alkali instead of for the same p_H. J. C. D.

A Tripeptide from Casein which contains Tryptophan. SIGMUND FRÄNKEL and ERNST NASSAU (*Biochem. Zeitsch.*, 1920, **110**, 287—298).—The tripeptide was prepared in the following way. Casein was digested with potassium hydroxide, and, when hydrolysis was complete, the solution was neutralised and acidified with sulphuric acid. A precipitate was formed. The filtrate was treated with 10% sulphuric acid and 10% mercuric sulphate, and the precipitate thus obtained decomposed with hydrogen sulphide in the presence of barium carbonate. It was then purified by various treatments with ethyl and methyl alcohol, and finally precipitated as the barium salt from methyl alcohol with ether. Analysis gave the formula $C_{50}H_{76}O_{20}N_{10}Ba$; decomp. 175—195°,

It was shown to contain $12H_2O$. The estimation of tryptophan in the barium compound showed that the tripeptide contained 2 molecules of it. It was also shown to contain one amino-group by Van Slyke's method. The tripeptide gave a very weak biuret reaction. On hydrolysing it with hydrochloric acid and on benzoylating it, *dl*-benzoylalanine, m. p. 163°, was obtained. The tripeptide has the formula $C_{25}H_{27}O_4N_5$, and is to be regarded as derived from 2 molecules of tryptophan and 1 molecule of alanine, with elimination of $2H_2O$. S. S. Z.

Preparation of Compounds of Nucleic Acid and Yohimbine which Dissolve Readily to Clear Solutions. Ernst Weinert (D.R.-P. 322996; from *Chem. Zentr.*, 1920, iv, 451).—Nucleic acid and yohimbehe bases are mixed in the presence of ammonia, or ammonium nucleate is treated with salts of yohimbine or the total base of the yohimbehe bark. *Yohimbine nucleate*, $C_{20}H_{30}O_4N_2,C_{40}H_{30}O_{26}N_{14}P_4$, is a yellowish- or greenish-white, amorphous powder, which has a feebly acidic taste and almost neutral reaction; it is readily soluble in water, and is expected to find therapeutic application. H. W.

Nuclein Metabolism. VII. Isolation of Crystalline Adenosinephosphoric Acid. S. J. Thannhauser (*Zeitsch. physiol. Chem.*, 1919, **107**, 157—164. Compare A., 1918, i, 316).—A mononucleotide, adenosinephosphoric acid, was obtained in the following way. The brucine salt of a triphosphonucleic acid (A., 1918, i, 47) was decomposed with ammonia, and the mixture of ammonium salts was further treated with lead acetate. The lead salts were then decomposed with hydrogen sulphide and the solution concentrated in a vacuum. After twenty-four hours, fine, colourless needles separated of adenosinephosphoric acid, m. p. 208° (decomp.), $[\alpha]_D^{20}$ −48·03°. The brucine salt has m. p. 180—182°. The nucleotide was hydrolysed with ammonia in the autoclave, and adenosinephosphoric acid, as well as the unchanged nucleotide, was obtained. S. S. Z.

The Swelling of Gelatin in Acids. W. R. Atkin (*J. Soc. Leather Tr. Chem.*, 1920, **4**, 248).—The quantity e (see T., 1916, **109**, 307) and the swelling of gelatin by solutions of various monobasic acids are functions of the hydrion concentration of the external acid solution, attain a maximum at $P_H = 2·4$, and minimum at $P_H = 4·6$, the isoelectric point of gelatin. D. W.

Production of a Contracting Clot in a Gel of Gelatin at the Isoelectric Point. Dorothy Jordan Lloyd (*Biochem. J.*, 1920, **14**, 584—585).—A sample of highly purified gelatin, prepared by a slight modification of the method of Dheré and Gorgolewski (A., 1910, i, 448), was dissolved in distilled water by heating, and cooled to 18°. The reaction of the solution at this temperature was $P_H = 6·09$. The gel which formed showed visible contraction after twenty-four hours. The experiments demonstrate that gelatin gels are unstable at the isoelectric point. Small quantities of sodium hydroxide have the same stabilising influence

subsequently the author and Bart have independently observed that the arsinic radicle becomes attached to the nucleus in place of the diazo-groups (D.R.-P. 250264 and 264924). It is now shown that the most favourable conditions for the production of phenylarsinic acid from a benzenediazonium salt and many of the nucleus-substituted derivatives are secured when the alkalinity of the solution is so regulated that reaction can occur in accordance with the scheme: $PhN_2Cl + AsO_3HK_2 = AsPhO_3HK + KCl + N_2$. The process then occurs spontaneously, and the diazo-compound is rapidly destroyed. In this manner, *o*-nitrobenzenediazonium chloride gives about 90% of the theoretical quantity of *o*-nitrophenylarsinic acid, but the amounts of arsenic-free by-products (azo-compounds, etc.) are more considerable in the cases of many other arsinic acids. In more strongly alkaline solution, the reducing action is more generally noticeable, and the yields of arsinic acids are lower. Poorer yields are also observed with a benzenediazonium salt in acid solution, but an acid medium is favourable when strongly acidic substituents are present in the benzene nucleus.

The theoretical interpretation of the reaction, in which the arsenic passes from the tervalent to the quinquevalent condition, offers considerable difficulties, but may be generally considered in conjunction with a number of other actions (formation of nitro-derivatives and sulphonic acids from diazo-compounds and nitrous or sulphurous acids and of alkyl-sulphonic, phosphinic, arsinic acids, etc., from alkyl haloids, and the salts of sulphurous, phosphorous, and arsenious acids, etc.) which have the common feature that an element passes from a lower to a higher valency by intramolecular atomic displacement and without the aid of an oxidising agent. The case of arsenious acid has been met, to some extent, by considering it to react in the form $O{:}AsH(OH)_2$ instead of $As(OH)_3$, but, in the author's opinion, a more general conception is obtained by adopting the following hypothesis. The acids H_2SnO_2, H_2SO_3, HNO_2, $[H_3PO_3]$, H_3AsO_3, and H_3SbO_3 can exist in modifications which contain one hydrogen atom in a peculiar form, and this labile variety becomes stabilised when the hydrogen atom is replaced by an organic radicle. Such replacement occurs when the salts of H_2SnO_2, H_2SO_3, HNO_2, (H_3PO_3), and H_3AsO_3 are treated with organic haloids, or when H_2SO_3, HNO_2, H_3AsO_3, or H_3SbO_3, as acids or salts, react with diazonium compounds, with evolution of nitrogen. The acids mentioned above yield additive compounds with alkyl haloids or diazo-compounds in the same manner as with oxygen, which, by elimination of alkali haloid or water and nitrogen, pass into derivatives of saturated acids with central atoms exhibiting higher valency. For the particular case under more immediate consideration, the following scheme is given:

$$PhN_2{\cdot}OH + As{\scriptstyle\begin{matrix}(OH)_2\\OK\end{matrix}} = {\scriptstyle\begin{matrix}PhN_2\\HO\end{matrix}}{>}As{<}{\scriptstyle\begin{matrix}(OH)_2\\OK\end{matrix}} = {\scriptstyle\begin{matrix}Ph\\O\end{matrix}}{>}As{<}{\scriptstyle\begin{matrix}OH\\OK\end{matrix}} + N_2 + H_2O.$$

In addition to the well-known arsenic-free by-products (such as benzene, azobenzene, hydrazobenzene, and aniline), others containing arsenic can also be isolated, the chief of which is *diphenylyl-4-arsinic acid*, $C_6H_4Ph\cdot AsO_3H_2$; since this substance is not obtained from benzenediazonium chloride and phenylarsinic acid, it must be assumed that a hydrogen atom of the benzene nucleus becomes labile at the moment at which the replacement of the diazo-residue by the arsinic group takes place, an explanation of the phenomenon being possibly found in Cain's method (T., 1907, **91**, 1049) of formulating diazo-compounds.

The preparation of the following individual compounds is described in detail: phenylarsinic acid, m. p. 156°; *phenyl*-p-*phenylenearsinic* [*diphenylyl*-4-*arsinic*] *acid*, m. p. not below 300°, corresponding chloride, m. p. 78—80° [Lettermann (*Inaug. Diss.*, Rostock, 1911) gives m. p. 275° and 74° respectively]; o-*nitrophenylarsinic acid*, yellow needles, m. p. about 232° (decomp.) when rapidly heated, obtained in 86% yield (the *magnesium* salt, woolly needles, is described); *m*-nitrophenylarsinic acid, shining leaflets, which pass into the anhydride at a temperature which entirely depends on the manner of heating, *2:3'-dinitrodiphenylyl-4-arsinic acid*, $NO_2\cdot C_6H_4\cdot C_6H_3(NO_2)\cdot AsO_3H_2$, pale brown powder, which slowly darkens above 230°, but is not molten at 260°; *p*-acetylaminophenylarsinic acid; *p*-aminophenylarsinic acid.

H. W.

Quantitative Studies in Chemotherapy. III. The Oxidation of Arsphenamine [Salvarsan]. CARL VOEGTLIN and HOMER W. SMITH (*J. Pharm. exp. Ther.*, 1920, **16**, 199—217. Compare this vol., i, 792).—The sodium salts of arsenious acid, methyl and ethyl arsenious oxide, phenyl- and diphenyl-arsenious oxide, and *p*-aminophenylarsenious oxide are relatively very stable towards atmospheric oxygen. Salvarsan [*3:3'-diamino-4:4'-di*hydroxyarsenobenzene] dihydrochloride, contrary to the prevalent views, is exceedingly stable towards atmospheric oxygen. The addition of alkali leads to a rapid increase in the rate of oxidation. The sodium salt of salvarsan is oxidised first to the corresponding oxide, and then to the quinquevalent compound. *m*-Amino-*p*-hydroxyphenylarsenious oxide ("arsenoxide") is oxidised only in alkaline solution. The nature of the process curve indicates that the reaction is catalysed by a reaction product.

Neoarsphenamine [neosalvarsan] shows rapid oxidation on exposure to air.

The nature and rate of oxidation of salvarsan and neosalvarsan to the corresponding oxides furnish an explanation of the increase in toxicity and trypanocidal activity of these compounds when their solutions are exposed to air. J. C. D.

The Colloidal Properties of Aqueous Solutions of "Salvarsan." Z. KLEMENSIEWICZ (*Bull. Soc. chim.*, 1920, [iv], **27**, 820—824).—The viscosity of aqueous solutions of salvarsan

increases from the moment of preparation, ultimately reaching an approximately constant value much higher than the initial value. The initial velocity of increase of the viscosity, as well as the final value of the viscosity, increase very considerably with the concentration of the solution. If a 10% solution, the viscosity of which has reached its final value, is diluted to 4%, a solution is obtained the viscosity of which is higher than the final viscosity of a 4% solution prepared directly from salvarsan. The viscosity of the diluted solution diminishes, however, on keeping to its correct value. Rise in temperature increases the rate at which a solution attains its final viscosity, but diminishes the value of the latter. The presence of acid or alkali has a marked effect on the viscosity of salvarsan solutions. W. G.

The Diazo-synthesis of Aromatic Stibinic Acids and the Investigation of their Polymeric Constitution. Aromatic Derivatives of Antimony Pentachloride and its Additive Compounds. HANS SCHMIDT (*Annalen*, 1920, **421**, 174—246. Compare Hasenbäumer, A., 1899, i, 209; Michaelis and Günther, A., 1911, i, 1056; Morgan aud Micklethwait, T., 1911, **99**, 2286; May, T., 1912, **101**, 1033; Grüttner and Wiernik, A., 1916, i, 96, 98).—Arylstibinic acids are readily prepared by the action of diazo-compounds on antimonious acid and its salts. In contrast to the similar reaction with arsenious acid, the method may even be applied iu concentrated alkaline solution, although when strongly acidic substituents are present in the nucleus, it is frequently preferable to operate in neutral or acid solution. The arylstibinic acids are shown, in general, to be derived from polymerised antimonic acids, and to be pronouncedly colloidal in their properties. The reactions indicated by the scheme

$$Ph{\cdot}SbO_2,nH_2O \longrightarrow Ph{\cdot}SbCl_2(\longrightarrow PhSb{:}SbPh) \longrightarrow Ph_2SbCl \longrightarrow Ph_3Sb,$$

have been realised, whereas previously they have only been accomplished with difficulty in the reverse direction.

Phenylstibinic acid is prepared by the gradual addition of a solution of antimony oxide in hydrochloric acid to benzenediazonium chloride, and subsequent treatment with an excess of sodium hydroxide solution, when copious evolution of nitrogen immediately occurs; alternatively, May's additive compound of benzenediazonium chloride and antimony trichloride is treated with an excess of cold dilute sodium hydroxide solution, whereupon nitrogen is gradually evolved. The crude product is best purified by conversion into the double salt of phenylstibine tetrachloride and ammonium chloride (see later), which is subsequently decomposed by water. Analyses of phenylstibinic acid give results in agreement with the formulæ $(3Ph{\cdot}SbO_2,H_2O)nH_2O$ and

$$(3Ph{\cdot}SbO_2,2H_2O)nH_2O,$$

but more information with regard to its constitution is derived from a study of its behaviour towards alkali. It is found that considerably less than one molecular proportion of alkali is required

to effect the solution of phenylstibinic acid, and that a solution prepared in this manner gradually becomes increasingly acid until a final point is reached. The phenomenon is caused by polymerisation and depolymerisation. The precipitated isolated phenylstibinic acid is a polymeric form, which is slowly decomposed to the unimolecular form in solution in the presence of alkali; the latter is only stable in the form of its alkali salts, and, when liberated, becomes again polymerised. Initial neutralisation occurs when the ratio Na : Sb is approximately 1 : 3, thus pointing to a trimolecular formula, probably

OH·SbOPh·O·SbOPh·O·SbOPh·OH,

but possibly admixed with OH·SbOPh·O·SbPh$(OH)_2$·O·SbOPh·OH; the final neutralisation value is somewhat less than that calculated for complete conversion into the unimolecular form, but this observation rests on the assumption that the colour change occurs with phenolphthalein when sodium hydroxide and the stibinic acid are mixed in molecular proportions. Phenylstibinic acid unites with hydrogen sulphide to yield pale yellow sulphides, which are decomposed when warmed, with partial formation of antimony sulphide. *Phenylstibine tetrachloride*, $PbSbCl_4$, is obtained when phenylstibinic acid is treated with concentrated hydrochloric acid and the solution evaporated at a moderate temperature; the freshly prepared substance has m. p. 60—65°, which rises to about 100° when it is preserved for some weeks in a vacuum, but partial decomposition takes place simultaneously. When heated, it dissociates into chlorine and dichlorophenylstibine, and the latter is further decomposed into chlorodiphenylstibine and antimony chloride. Its solution in concentrated hydrochloric acid unites with ammonium chloride, giving $SbCl_5PhNH_4$, pale yellow, voluminous powder, which does not change below 260°, and similar *salts* are formed with the hydrochlorides of aniline, dimethylaniline, pyridine, quinoline, dicyandiamidine, guanidine, carbamide, ethylaniline, and allylamine; methyl- and ethyl-amines behave somewhat differently, yielding precipitates, which are initially white, but rapidly become yellow.

m-Nitrophenylstibinic acid, $[3(NO_2·C_6H_4·SbO_2),2H_2O],3H_2O$ (compare Morgan and Micklethwait, *loc. cit.*), is prepared by the nitration of phenylstibinic acid by nitric acid (D 1·515), or by nitric and sulphuric acids at the ordinary temperature; it is more rapidly depolymerised by alkali than the parent acid. The corresponding *chloride*, $NO_2·C_6H_4·SbCl_4,H_2O$, m. p. 140° (decomp.), and *double ammonium chloride*, colourless crystals ($+\frac{1}{2}H_2O$), which soften above 235°, are described. The acid is also obtained, but less advantageously, by the action of *m*-nitrobenzenediazonium chloride on potassium antimonyl tartrate in faintly acid solution. *o-Nitrophenylstibinic acid* forms a pale yellowish-brown powder, which remains unchanged below 285°, and with alcoholic hydrogen chloride gives the corresponding *chloride*, crystalline leaflets, m. p. about 127°. p-*Chlorophenylstibinic acid*,

$[3(C_6H_4Cl·SbO_2),2H_2O],3H_2O$,

osely resembles phenylstibinic acid; it is converted by hydro-
ıloric acid into an unstable, yellow chloride, which gives the
ırresponding *double ammonium chloride*, lemon-yellow precipitate,
hich remains unchanged below 250°. p-*Chloro*-m-*nitrophenyl-*
ibinic acid forms an almost colourless powder, which is unaltered
›low 285°; *the chloride*, $NO_2 \cdot C_6H_3Cl \cdot SbCl_4,5H_2O$, *has m. p. about*
)° after previous softening, whilst the *monohydrate* softens at
›out 122°; the *double ammonium chloride*,

$$(NO_2 \cdot C_6H_3Cl \cdot SbCl_4)_2NH_3,8H_2O,$$

ırms a colourless, voluminous precipitate, m. p. above 220°
lecomp.) after previous softening. With the acids in general, it
found that the presence of acid substituents causes a marked
:celeration of the process of hydration, whilst the basic amino-
·oup effects a distinct retardation. m-*Nitro*-p-*hydroxyphenyl-*
ibinic acid, $[3(NO_2 \cdot C_6H_3(OH) \cdot SbO_2),2H_2O],5H_2O$, prepared by
ıe action of concentrated aqueous potassium hydroxide on the
ırresponding chloro-acid, is a yellowish-brown powder, which
·adually darkens above 230°; the corresponding *chloride* and
ıuble ammonium chloride are stable substances. *p*-Anisylstibinic
:id gives a remarkably unstable chloride.

The possibility of preparing the phenylstibinic acids readily and
good yield has rendered the isolation of the antimonylaryls a
ımparatively easy matter, and many of them are described. In
›neral, they are amorphous substances, in which the acidic
roperties of antimony oxide are no longer manifest; with halogen
:ids, on the other hand, they form characteristic compounds,
rSbHal$_2$, in which the halogen is either not hydrolytically
›moved or is replaced with greater difficulty than in antimony
ıloride. When heated alone or in certain solvents, they tend to
›compose, according to the scheme Ph·SbO ⟶ $(Ph_2Sb)_2O$ ⟶
h$_3$Sb, the action being both positively and negatively catalysed
7 a number of reagents in an apparently irregular manner. The
ıysiological action of derivatives of tervalent differ markedly
om those of quinquevalent antimony, since the former vigorously
:tack the skin and mucous membrane. Phenylstibine oxide,
bPhO, voluminous powder, which softens at 153—154° (Hasen-
iumer, *loc. cit.*, gives m. p. 150°), is prepared by the action of
ılphur dioxide in the presence of a little sodium iodide on an
e-cold aqueous methyl-alcoholic solution of phenylstibinic acid
ıd concentrated hydrochloric acid; the *iodide*, $SbPhI_2$, forms
›lden-yellow needles, m. p. 69°, whilst the chloride, colourless
›edles or plates, has m. p. 62° (Hasenbäumer gives m. p. 58°,
hilst Grüttner and Wiernick describe the substance as an oil).
.ddition of water to the alcoholic solution of the haloids causes
ıe formation of oxyhaloids. Energetic reduction of phenyl-
:ibinic acid or phenylstibine oxide leads to the formation of *stibio-*
enzene, PhSb:SbPh, *brown, amorphous powder, which gradually*
arkens above 160°, and finally softens to a black mass, and
extraordinarily susceptible to atmospheric oxidation; the proper-
es of the product depend considerably on the mode of reduction

which is preferably effected with sodium hypophosphite in acetone-glacial acetic acid solution.

m-Nitrophenylstibinic acid is reduced by stannous chloride and saturated alcoholic hydrogen chloride to m-*aminophenyldichlorostibine hydrochloride*, $SbCl_2\cdot C_6H_4\cdot NH_2,HCl$, colourless needles, m. p. 218° (decomp.), which is converted by sodium iodide into m-*aminophenyldi-iodostibine hydriodide*, golden-yellow precipitate, m. p. 160° (decomp.). Cautious treatment with water and ammonia transforms the chloride into *m*-aminophenylstibine oxide, colourless, amorphous powder, which shrinks at about 170° and readily undergoes decomposition; it is oxidised by hydrogen peroxide to *m*-aminophenylstibinic acid,

$$[3(NH_2\cdot C_6H_4\cdot SbO_2),H_2O],4H_2O$$

(the *sodium* salt and the *sulphate* are described), which is transformed by hydrochloric acid into m-*aminophenylstibine tetrachloride hydrochloride*, colourless crystals ($+1\cdot5H_2O$), which blacken above 190°. (Some of these substances have been described previously by May, and the discrepancies between his data and those of the present author are due to the contamination of May's products with di- and tri-antimony derivatives.) Energetic reduction with sodium hypophosphite converts *m*-aminophenyldichlorostibine hydrochloride into mm′-*diaminostibiobenzene*, dark brown powder, which shrinks to a black mass above 120°, and is very readily oxidised. p-*Chloro*-m-*aminophenyldichlorostibine hydrochloride* forms colourless needles, m. p. about 153° (decomp.), and is converted by cold dilute ammonia into p-*chloro*-m-*aminostibine oxide*.

A considerable number of diarylantimony-compounds are described (compare Michaelis and Reese, A., 1886, 885; Michaelis and Günther, *loc. cit.*); the diarylstibinic acids are prepared by the oxidation of the diarylstibine oxides or by the action of antimonylaryls on diazo-compounds, $Ar^IN_2Cl+Ar^{II}SbO+2KOH = Ar^IAr^{II}SbO\cdot OK+N_2+KCl$, the latter procedure permitting the introduction of dissimilar radicles into the acid molecule. They differ considerably from the monoarylstibinic acids in their tendency towards polymerisation, and their behaviour towards alkali does not enable such definite conclusions to be drawn as in the case of the simpler compounds.

Diphenylstibine oxide, $O(SbPh_2)_2$, m. p. 78—80°, is prepared by heating phenylstibine oxide in a current of dry carbon dioxide at 100°, or by the action of tartaric acid on a solution of the substance in glacial acetic acid at the ordinary temperature; it is reduced by hypophosphorous acid to a yellow *compound*, presumably tetraphenyldistibine, $Ph_2Sb\cdot SbPh_2$, converted by hydrochloric acid into chlorodiphenylstibine, m. p. 68°, and oxidised by hydrogen peroxide in alcoholic alkaline solution to diphenylstibinic acid, m. p. about 285°. m-*Aminodiphenylstibinic acid*,

$$NH_2\cdot C_6H_4\cdot SbPhO\cdot OH,H_2O,$$

from diazotised aniline and dichloro-*m*-aminophenylstibine hydrochloride in the presence of excess of alkali, is a colourless powder

which softens at about 200°, and is readily converted into the *chloride*, which gradually darkens when heated above 200°. Chloro-*mm'*-diaminodiphenylstibine hydrochloride, colourless needles, m. p. 215° (decomp.) (compare Morgan and Micklethwait, *loc. cit.*), yields hydroxy-*mm'*-diaminodiphenylstibine which softens indefinitely above 70°, and is oxidised by hydrogen peroxide to *mm'*-diaminodiphenylstibinic acid,

$$(NH_2{\cdot}C_6H_4)_2{:}SbO{\cdot}OH,0{\cdot}5H_2O,$$

decomp. about 230° (*mm'-diaminodiphenylstibine chloride hydrochloride* remains unchanged below 250°).

Triphenylstibine, m. p. 53°, results when phenylstibine oxide is heated in a stream of dry carbon dioxide at 180—200°. Tri-*m*-aminotriphenylstibine exists in an amorphous, hydrated form ($+0{\cdot}5H_2O$), which softens above 80°, and a crystalline variety m. p. 124°. The former can be converted into the latter by crystallisation from alcohol, the reverse change being effected by solution in hydrochloric acid and precipitation with ammonia.

The estimation of antimony is effected by one of the following methods. Arylstibine oxides and triarylstibines, which contain an amino-group attached to the benzene nucleus, can frequently be directly titrated with iodine in very dilute faintly acid solution. If the stibine oxide is devoid of a group conferring the property of solubility in water, a suitable bicarbonate-alkaline solution can generally be obtained with the aid of tartaric acid and organic solvents. Alternatively, about 1/1000 molecule of the substance is mixed in a Kjeldahl flask with sodium chloride (0·2 gram) and sodium hydrogen sulphate (3 grams), and boiled during an hour with a mixture of nitric acid (D 1·49; 1·5 c.c.) and concentrated sulphuric acid (10 c.c.). After cooling, ammonium sulphate (1 gram) is added, and the mixture is boiled for thirty minutes to remove nitric acid; it is subsequently diluted to about 300 c.c. and, after addition of 5*N*-hydrochloric acid (20 c.c.), is reduced with sulphur dioxide and potassium bromide. The antimony is finally estimated by titration with *N*/10-iodine in bicarbonate alkaline solution. H. W.

Action of Mercaptans and Hydrogen Sulphide on *o*-Chloromercuribenzoyl Chloride. GEORG SACHS (*Ber.*, 1920, **53**, [*B*], 1737—1745).—*o*-Chloromercuribenzoyl chloride can possibly react with the sulph-hydryl group in accordance with either of the schemes:

$$ClHg{\cdot}C_6H_4{\cdot}COCl + HS{-} = ClHg{\cdot}C_6H_4{\cdot}CO{\cdot}S{-} + HCl$$

and $ClHg{\cdot}C_6H_4{\cdot}COCl + HS{-} = {-}S{\cdot}Hg{\cdot}C_6H_4{\cdot}COCl + HCl$. With mercaptans, the reaction follows the first course, with hydrogen sulphide the second. An explanation of the failure of the –HgCl group to react with mercaptans is found in the observation that whilst *o*-chloromercuribenzoic acid and phenylmercurichloride do not react with mercaptans in acetone solution, even when heated on the water-bath, sodium chloromercuribenzoate and ethyl

mercaptan readily yield ethylthiomercuribenzoic acid at the ordinary temperature:

$$ClHg\cdot C_6H_4\cdot CO_2Na + HSEt = SEt\cdot Hg\cdot C_6H_4\cdot CO_2H + NaCl.$$

Reaction therefore appears to take place only when the liberated hydrochloric acid is immediately neutralised. This circumstance, taken in conjunction with signs of ready hydrolysis of the mercapto-acids, indicates that this new class of substances is to be regarded as salts of a very weak acid, in which the specific relationship of mercury to sulphur does not play an important part. Reaction between mercaptans and phenylmercurichloride or chloromercuribenzoic acid takes place at 150°, and leads to rupture of the mercury–carbon bond: $ClHg\cdot C_6H_4\cdot CO_2H + HSEt = Ph\cdot CO_2H + ClHg\cdot S\cdot Et$. Similar fission occurs when sulphidomercuribenzoyl chloride is treated with boiling methyl alcohol; mercuric sulphide is precipitated, as is usual with this type of sulphide, and, in addition, the remainder of the molecule decomposes smoothly under the influence of the liberated hydrogen chloride.

$$S(Hg\cdot C_6H_4\cdot COCl)_2 + 2MeOH = ClHg\cdot C_6H_4\cdot CO_2Me + Ph\cdot CO_2Me + HgS + HCl.$$

The following substances are described: *o-chloromercuribenzoyl chloride*, needles, which melt incompletely at 173·5°, is prepared, together with small amounts of an amorphous substance, by the action of thionyl chloride on hydroxymercuribenzoic anhydride, $C_6H_4<{CO \atop Hg}>O$ (it is remarkable that *o*-chloromercuribenzoic acid does not react with thionyl chloride, whilst *o*-ethylthiomercuribenzoic acid gives chloromercuribenzoic acid and smaller amounts of highly decomposed substances); *sulphidomercuribenzoyl chloride*, $S(Hg\cdot C_6H_4\cdot COCl)_2$, pale yellow precipitate, which does not melt below 230°, obtained by the interaction of chloromercuribenzoyl chloride and hydrogen sulphide in dry ethereal solution; methyl *o*-chloromercuribenzoate, m. p. 181·5—182° (Schrauth, Schoeller, and Hueter, this vol., i, 455, give m. p. 142—162°), which after some months had fallen to 149—149·5°, and could not then be restored to its original value; *ethyl o-chloromercurithiobenzoate*, $ClHg\cdot C_6H_4\cdot CO\cdot SEt$, yellow, microscopic, rhombic leaflets, m. p. 142·5—144·5°; ethylthiomercurichloride; *ethylthiomercuribenzoic acid*, m. p. 138·5—140° to a turbid liquid, which immediately blackens, owing to separation of mercuric sulphide.

H. W.

Mercury Derivatives of Substances with Multiple Bonds. IV. W. MANCHOT, F. BÖSSENECKER, and F. MÄHRLEIN (*Annalen*, 1920, **421**, 316—330).—The mercuration of benzene derivatives which contain a double bond in the side-chain has been investigated; the results obtained are similar to those recorded with ethylene (this vol., i, 720), and thus further confirm the authors' conclusion that these substances are to be regarded as additive compounds.

Safrole is readily dissolved by aqueous mercuric acetate solution at 50°, and the product is converted by aqueous sodium chloride into the *substance*, $CH_2O_2{:}C_6H_3\cdot CH_2\cdot CH{:}CH_2,HgCl\cdot OH$, colourless,

well-defined, stable, monoclinic prisms, m. p. 136—137°, which is immediately decomposed by dilute hydrochloric acid, with regeneration of safrole; the corresponding *bromide*, colourless, silky needles, m. p. 144—145°, and the *iodide*, slender needles, m. p. 152·5°, are similarly prepared. The mercury atom is comparatively firmly retained in all these compounds. The free *base* is readily obtained in aqueous solution by the action of silver oxide on the bromide; it is faintly alkaline to litmus, but does not give a coloration with phenolphthalein. In a similar manner, eugenol methyl ether yields the *compound*, $C_{11}H_{15}O_3 \cdot HgCl$, colourless needles, m. p. 112·5°, but the preparation is rendered unusually difficult by the formation of smeary masses. Eugenol itself, on the other hand, does not yield a well-defined product when molar proportions of the components are taken; when, however, three molecules of mercuric acetate react with one molecule of eugenol, a very sparingly soluble *product* is obtained, which contains two atoms of mercury (a similar *substance* can also be prepared from safrole). Mercuration of phenylethylene gives more complex products, investigation of which is not quite completed; it is, however, established that addition of basic mercury salts occurs, and that the products, in part at any rate, do not retain the mercury firmly. Styrenes, which contain a terminal methyl group in the side-chain (*iso*safrole, *iso*eugenol), behave differently, causing reduction of the mercury salt, as does β-methylbutylene.

Estimation of mercury is conveniently effected as follows. The substance is gently boiled under a reflux condenser with hydrochloric acid (20%; 20 c.c.) and concentrated hydrogen peroxide (3 c.c.) during three to four hours. Organic matter is removed by filtration, and the residue is thoroughly washed. The mercury is precipitated in the filtrate by hydrogen sulphide. The precipitated mercuric sulphide is collected in a Gooch crucible, and freed from organic matter and uncombined sulphur by being washed successively with hot water, alcohol, pyridine, alcohol, warm carbon disulphide, alcohol, and ether; it is dried at 110° until constant in weight. The process gives very accurate results, and shows that the high values obtained previously are mainly due to contamination of the mercuric sulphide by organic matter.

H. W.

Physiological Chemistry.

A Method for the Graphic Representation of Chemical Compounds and Reactions. OTTO LIESCHE (*Biochem. Zeitsch.*, 1920, **105**, 282—304).—A theoretical paper dealing with the application of the graphic representation of chemical compounds and reactions to biochemistry. S. S. Z.

Catalysis. VII. Temperature-coefficient of Physiological Processes. NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 44—49).—Physiological processes take place mostly in heterogeneous media. The Brownian movement of the colloid particles present in the reacting substances does away with the diffusion layer characteristic of heterogeneous reactions, and makes the physiological reactions similar to positively catalysed reactions taking place in homogeneous media. Consequently, the temperature-coefficients of physiological processes, instead of being small (about 1·2), are usually greater than 2 for a rise of 10°. The spontaneous destruction of certain toxins is greatly influenced by temperature, a factor of importance in fever, when the poison is destroyed very rapidly. Before the destructive effect of temperature sets in, the Arrhenius formula connecting temperature and reaction velocity is generally applicable to physiological processes (compare A., 1919, ii, 404). J. R. P.

The Presence of Glycuronic Acids in Human Blood. Preliminary Note. WILHELM STEPP (*Zeitsch. physiol. Chem.*, 1919, **107**, 264—268).—Several samples of blood from normal, diabetic, and nephritic patients were examined for glycuronic acid by the naphtharesorcinol reaction. All the samples examined gave a positive reaction, the blood of the nephritic patients in the azotæmia stage giving the most intense coloration. The reaction in the case of the diabetics showed varying intensity. The orcinol and phloroglucinol reactions were also employed in the latter case. S. S. Z.

The Reducing Substances of Blood. Comparative Estimations of "Blood Sugar" by means of Reduction, Polarisation, and Fermentation in Several Cases of Diabetes and Nephritis. WILHELM STEPP (*Zeitsch. physiol. Chem.*, 1919, **107**, 29—44).—Estimations of blood sugar in the blood of diabetic and nephritic patients with Lohnstein's "precision fermentation saccharimeter" give figures similar to those obtained by polarimetric estimations. As the reducing power shown by blood is always in excess of that theoretically required by the amount of blood sugar estimated polarimetrically, it is to be deduced that reducing substances other than dextrose are responsible for this. Certain samples of blood of diabetic patients, when concentrated, give a lower reducing value than the equivalent quantity of original blood, which suggests that some of the reducing substances are volatile. In one instance, the reduction of Fehling's solution by the distillate has actually been established. As the concentrated blood samples still show a higher reducing power than that expected from the polarisation and fermentation figures, it may be assumed that, besides volatile, there are non-volatile reducing substances in blood which cannot be identified with dextrose. S. S. Z.

The Physiological Distribution of Sugar in Plasma and Corpuscles. R. BRINKMAN and (FRL.) E. VAN DAM (*Biochem. Zeitsch.*, 1920, **105**, 93—95).—The erythrocytes of human and frog's blood do not contain sugar; they only become permeable to it after the blood has clotted. Corpuscles, however, in blood which is prevented from clotting by sodium fluoride, oxalate, or hirudin become permeable to sugar. This is explained by the fact that the early phases of clotting are not hindered by these reagents.

S. S. Z.

The Nomenclature of the so-called Accessory Food Factors (Vitamins). JACK CECIL DRUMMOND (*Biochem. J.*, 1920, **14**, 660).—It is suggested that the name vitamin be employed for these unidentified substances, and that they be individually referred to as vitamin-*A*, -*B*, -*C*, etc. Dropping the final "e" in the original word vitamine, introduced by Funk, removes the objections to that word. J. C. D.

Researches on the Fat-soluble Accessory Substance. III. Technique for carrying out Feeding Tests for Vitamin-*A* (Fat-soluble-*A*). JACK CECIL DRUMMOND and KATHARINE HOPE COWARD (*Biochem. J.*, 1920, **14**, 661—664).—Great care should be employed to ensure that the basal diet is free from this vitamin.

J. C. D.

Researches on the Fat-soluble Accessory Substance. V. The Nutritive Value of Animal and Vegetable Oils and Fats Considered in Relation to their Colour. JACK CECIL DRUMMOND and KATHARINE HOPE COWARD (*Biochem. J.*, 1920, **14**, 668—677).—No hard-and-fast line can be drawn between the animal and vegetable oils and fats when their value as a source of vitamin-*A* is considered. As a class, the animal fats are superior in this respect to the vegetable oils, but some members of the latter class, for example, palm oil, may be valuable sources of the vitamin. The presence of lipochrome pigments cannot be regarded as a certain indication of the presence of the vitamin-*A*. The nutritive value of an animal oil is largely dependent on the diet which the animal has received. Both animal and vegetable oils and fats probably lose vitamin during purification and refining.

J. C. D.

Cuorin. HUGH MACLEAN and WILLIAM JAMES GRIFFITHS (*Biochem. J.*, 1920, **14**, 615—617).—Cuorin, described by Erlandsen (A., 1907, i, 371), is not a chemical unit, but results from decomposition taking place in the tissues during the processes utilised for the extraction of the lipins.

The only phosphatides present in animal tissues are lecithin, kephalin, and sphingomyelin. J. C. D.

Primary and Secondary Phenol Reaction. Mutual Antagonism of α-Naphthol and *p*-Phenylenedimethyldiamine in Daphnideæ. W. LOELE (*Zentr. allg. Pathol. pathol. Anat.*, **30**, 614—617; from *Chem. Zentr.*, 1920, iii, 493).—Accord-

ing to Gierke and Graeff, naphthol dissolves the labile oxydases (protective colloids of the muscles against foreign substances). These oxydases, which are probably cyclic amines with aldehydic character, are termed aldamines by the author. They are particularly noticeable where the cells have a markedly *protective* character. They may be classified as: (1) primary aldamines (*a*) yielding the naphthol reaction without treatment with formaldehyde, and (*b*) giving a positive naphthol reaction only after addition of formaldehyde, and (2) secondary aldamines showing (*a*) granular reaction, and (*b*) nucleus reaction. Substances belonging to the first group are found in the granula of α- and δ-leucocytes and in the cell of the snail, and do not appear to be associated with any particular form of cell. Members of the sub-group, *b*, are present in the mucus cells of the black snail. The secondary aldamines, which are formed by the action of primary aldamines, have the greater importance. H. W.

The Distribution of Inorganic Iron in Plant and Animal Tissues. HENRY WALLACE JONES (*Biochem. J.*, 1920, **14**, 654—659).—By microchemical methods, the author has traced the occurrence of inorganic iron in a large number of organisms. Inorganic iron is more widely distributed throughout animal and plant tissues than is generally realised, and the lower organisms in both cases give the reaction more markedly than the higher ones. Aquatic animals contain more than land animals, and fœtal tissues are richer than adult tissues. J. C. D.

Biochemical Studies on Marine Organisms. I. The Occurrence of Copper. WILLIAM C. ROSE and MEYER BODANSKY (*J. Biol. Chem.*, 1920, **44**, 99—112).—Numerous analyses are recorded, and it is believed that copper is a normal, and possibly an essential, constituent of marine animals.
J. C. D.

The Distribution of Zinc in the Organism of the Horse. GABRIEL BERTRAND and R. VLADESCO (*Compt. rend.*, 1920, **171**, 744—746).—All the organs and tissues of the horse contain notable proportions of zinc, the amounts found varying from 3—36 mg. per 100 grams of fresh material. Not only does the amount of zinc vary considerably from one organ or tissue to another, but also from one animal to another. W. G.

Excretion of Formic Acid from the Human Organism after the Administration of Methyl Alcohol, Hexamethylenetetramine, Sodium Formate, Sodium Lactate, and Dextrose. W. AUTENRIETH (*Arch. Pharm.*, 1920, **258**, 15—33).—Formic acid is a normal and fairly constantly occurring constituent of human urine, varying in quantity within somewhat wide limits with different individuals and with varying diet, but from 0·5—0·65 gram per forty-eight hours, or an average of about 0·28 gram per day, may be regarded as a normal amount. Adminis-

tration of methyl alcohol causes a notable increase in the formic acid excreted, particularly on the third and fourth day following, the total excess over the normal representing about 5% of the methyl alcohol taken. The mere presence of formic acid in the urine is accordingly insufficient to establish methyl alcohol poisoning. In such a case, a quantitative examination indicating something of the order of 1 gram of formic acid per day is essential. In no case was formaldehyde found in the urine after the administration of methyl alcohol, although possibly traces of the latter might be found unchanged. This, together with the fact that, after the administration of hexamethylenetetramine (urotropine), large quantities of formaldehyde, but no increase in the amount of formic acid, were found in the urine, shows that formaldehyde is not, as has been supposed, an intermediate product of oxidation in the animal organism. Formic acid, administered as its sodium salt, underwent partial combustion, 18% only being found unchanged in the urine. Neither sodium lactate nor dextrose caused any abnormal increase in the excretion of formic acid, even when administered in large quantities. G. F. M.

The Physical Theory of Pharmacological Actions. I. TRAUBE (*Biochem. Zeitsch.*, 1920, **105**, 115—116).—A reply to Heubner (this vol., i, 791). S. S. Z.

The Narcosis Theory. ERICH KNAFFL-LENZ (*Biochem. Zeitsch.*, 1920, **105**, 88—92).—A reply to Winterstein (A., 1917, i, 68) and Traube (*Pflüger's Archiv*, 1919, **176**, 72). S. S. Z.

Fate of β-Naphthylamine in the Organism of the Dog. ENGEL (*Zentr. Gewerbehyg. Unfallverhüt.*, **8**, 816; from *Chem. Zentr.*, 1920, iii, 495).—β-Naphthylamine hydrochloride (1·0 and 0·5 gram) was administered to two dogs which were in a condition of nitrogen equilibrium and had a constant nitrogen and sulphur elimination. Signs of illness were not observed. After the injection, the amounts of ethylsulphuric acid and glycuronic acid in the urine were increased, and this lasted for five to six days. The ratio of the two acids indicated that much the greater part of the amine is eliminated in conjunction with the ethylsulphuric acid, at any rate in the case of carnivorous animals. In one experiment with a carbohydrate diet, only one-fourth of the amine was associated with ethylsulphuric acid, the remainder with glycuronic acid. The increment in the amounts of the two acids eliminated, amounted in one experiment to 0·725 and 0·486 gram respectively. Assuming that only aminonaphthols are formed, this would correspond with 1·444 grams of β-naphthylamine, which is more than was actually administered; it appears, therefore, that dihydroxynaphthylamines are also formed. Unchanged β-naphthylamine could not be detected in the urine. H. W.

A Toxicological Study of some Alcohols, with especial reference to Isomerides. DAVID I. MACHT (*J. Pharm. expt. Ther.*, 1920, **16**, 1—10).—The toxicity of the normal aliphatic

alcohols, methyl, ethyl, butyl, and amyl, increases with their place in the homologous series.

Secondary propyl, butyl, and amyl alcohols were found to be less toxic than the corresponding primary alcohols.

In discussing the toxicity of alcohols, a distinction should be drawn between the acute or immediate, and the secondary or remoter, effects of the drugs. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

The Production of Acetaldehyde by certain Pentose Fermenting Bacteria. W. H. Peterson and E. B. Fred (*J. Biol. Chem.*, 1920, **44**, 29—46).—In the fermentation of carbohydrates by three types of pentose-fermenting organisms (an organism related to the colon-ærogenes group, *Bacillus acetoethylicum*, and *Lactobacillus pentoaceticus*), acetaldehyde is produced when a fixative, such as sodium or calcium bisulphite, is added. The maximum yield is from xylose, but the amount found is proportional to the amount of fixative added. The production of acetaldehyde is correlated with the production of alcohol. An increase in the former results in a decrease in the latter. The production of acetaldehyde is associated with a high production of volatile acid. These results illustrate the intimate relations which exist between the balanced processes of oxidation and reduction in the fermenting solution.

The production of acetaldehyde by the acetone-forming organism, *B. acetoethylicum*, is of particular interest, since it is possible that, through condensation of the aldehyde and subsequent processes of oxidation and decarboxylation, the acetone is formed.

An attempt to correlate the production of acetaldehyde with Neuberg's theory, that pyruvic acid is an intermediate product in sugar fermentation, did not give conclusive results. Pyruvic acid and its sodium salt are fermented to a greater or less extent by all three types of bacteria. Among the products formed are carbon dioxide, hydrogen, and a volatile acid. These products were also formed when pyruvic acid was fermented in the presence of sodium sulphite, but no trace of acetaldehyde was found. J. C. D.

New Methods of Analysis of Hydrocarbons with the Aid of Bacteria. Jenő Tausz and Márta Peter (*Centr. Bakt. Par.*, 1919, II, **49**, 497—554).—The authors have isolated from garden soil three new bacteria, namely, *Bacterium aliphaticum*, *B. aliphaticum liquefaciens*, and *Paraffin bacterium*. The actions of these bacteria on pure synthetic hydrocarbons and on mixtures

of paraffins and naphthenes have been investigated, the hydrocarbons tested comprising *n*-hexane, *n*-octane, $\beta\eta$-dimethyloctane, hexadecane, triacontane, and tetratriacontane; *n*-hexylene, *n*-octylene, and hexadecylene; *cyclo*hexane, methyl*cyclo*hexane, 1 : 3-dimethyl*cyclo*hexane, 1 : 3 : 4-trimethyl*cyclo*hexane, and *tricyclo*decane; benzene, toluene, *m*- and *p*-xylenes. The hydrocarbons were used as the sole source of carbon in solutions of inorganic nutrient materials.

B. aliphaticum attacks all the paraffins mentioned, and also *n*-octylene and hexadecylene, but not *n*-hexylene, naphthenes, or aromatic hydrocarbons. *B. aliphaticum liquefaciens* behaves exactly similarly. The *Paraffin bacterium* attacks hexadecane, triacontane, tetratriacontane, and hexadecylene, but not *n*-hexane, *n*-octane, hexylene, octylene, naphthenes, or benzene derivatives. The hydrocarbons attacked are destroyed completely by the bacteria, even when unattacked naphthenes are present. The organisms were employed in the analyses of various mixtures of hydrocarbons. T. H. P.

Inhibitory Action of Paratyphoid Bacilli on the Fermentation of Lactose by Bacillus coli. I. THEOBALD SMITH and DOROTHEA E. SMITH (*J. Gen. Physiol.*, 1920, **3**, 21—33).—Bacteria of the paratyphoid group can be divided into two classes, according to whether they inhibit the formation of gas from lactose by *Bacillus coli* or not. The production of acid is not interfered with. The experiments support current theories, which hold that the acid-producing and gas-producing entities in cultures are distinct. J. C. D.

Production of Indole by the Pfeiffer Bacillus. MARCEL RHEIN (*Compt. rend. soc. biol.*, 1919, **82**, 138—139).—The production of indole (mauve colour with dimethylaminobenzaldehyde and hydrochloric acid, violet tint with formaldehyde and sulphuric acid, blue colour with sodium nitroprusside, potassium hydroxide, and acetic acid), with accompanying characteristic odour, was noted in the case of abundant cultures of the Pfeiffer bacillus, but not detected in all cases. CHEMICAL ABSTRACTS.

Synthesis of Tryptophan by certain Bacteria and the Nature of Indole Formation. WILLIAM JAMIESON LOGIE (*J. Path. Bact.*, 1920, **23**, 224—229).—Certain gram-negative bacilli have the power to synthesise tryptophan when growing in protein-free media. This is in support of the view of the vegetable nature of bacteria. The addition of dextrose to a living culture of *Bacillus coli* causes the rapid disappearance of the indole already formed. This seems to indicate that the effect of the dextrose is to cause increased demand for indole on the part of the organism, and not merely, by the development of acidity, to prevent the splitting off of indole from the peptone. On this hypothesis, indole "formation" is a consequence rather of diminished use of indole

as tryptophan than of special formation by the organism. The splitting off of indole appears to be a reversible chemical change.

The difference between *B. coli* and *B. typhosus* with respect to indole formation on re-absorption is most probably due to the fact that *B. coli* possesses an enzyme which enables it to split off and utilise the open-chain (alanine) portion of the tryptophan molecule.

J. C. D.

The Effect of Certain Environmental Conditions on the Rate of Destruction of Vanillin by a Soil Bacterium. WILLIAM J ROBBINS and A. B. MASSEY (*Soil Sci.*, 1920, **10**, 237—246).—The particular bacterium used was one from an Alabama soil. In culture solutions, very slight concentrations of hydrochloric acid inhibited its action on vanillin, but the bacterium was not so sensitive to alkali. Aeration favoured the destruction of vanillin by the organism. In culture solutions containing calcium superphosphate, sodium nitrate, and potassium sulphate, either singly or in combination, the organism was most active in those solutions rich in calcium superphosphate and least active in the solutions rich in potassium sulphate. The presence of dextrose had no marked effect on the rate of destruction of vanillin by the organism.

W. G.

Yeast Nutrition and Fermentation. Does Development of Yeast Occur without Fermentation of Sugar? TH. BOKORNY (*Centr. Bakt. Par.*, 1920, ii, **50**, 23—33).—The author finds that it is possible for considerable increase of yeast to occur in solutions containing no trace of sugar. Besides the ordinary fermentable sugars, rhamnose, arabinose, lactose, peptone, asparagine, and other amides, tartaric, acetic, and citric acids, and, under certain conditions, glycerol, all serve to supply yeast with the carbon necessary for its growth. Between the nitrogenous constituents of the nutrient solution and the fermentation of the sugar present, the sole connexion existing is that plentiful and suitable nitrogenous nutrition gives rise to much yeast, and thus to much zymase. Fermentation is not, at any rate when access of air is permitted, a vital necessity for yeast, but it is of advantage in that it retards the development of bacteria, and, further, brings the yeast into increased contact with the nutrient materials of the liquid.

T. H. P.

Is Fermentation of Sugar by Yeast due Solely to Zymase? J. GIAJA (*Compt. rend. soc. biol.*, 1919, **82**, 804—806). —Yeast lost 86% and 94% of its fermentative power when treated with toluene for thirty and sixty minutes, respectively, after attaining its maximal fermentative activity in the presence of sugar. The residual 6% of "zymase" (which remained practically intact for a long time) is practically identical in amount with that possessed by yeast treated as above during rest. Yeast from which the enveloping membrane had been dissolved by the action of the

digestive fluid of *Helix pomatia* likewise lost most of its fermentative power when treated with toluene. The above loss of fermentative power cannot plausibly be attributed to destruction of zymase by the action of endotrypsin as suggested by Buchner. The author concludes that only approximately 5% of the fermentative activity of yeast can be attributed to zymase. CHEMICAL ABSTRACTS.

The Effect of Pyruvates, Aldehydes, and Methylene-blue on the Fermentation of Dextrose by Yeast Juice and Zymin in the Presence of Phosphate. ARTHUR HARDEN and FRANCIS ROBERT HENLEY (*Biochem. J.*, 1920, **14**, 642—653).—The facts that the activating effect both of α-keto-acids and of aldehydes is chiefly manifested at the commencement of the reaction, and that the experiments both of Oppenheimer (A., 1915, i, 358) and Neuberg (A., 1915, i, 1043; 1918, i, 469) were made with maceration extracts which contain a large amount of mineral phosphate, and that the effect was less marked with lævulose than with dextrose, led the authors to inquire whether the action was a general stimulation of the fermentation process or a more specific acceleration of the reaction in presence of free mineral phosphate.

It has been found that an aldehyde when added to fermenting mixtures of yeast juice or zymin (acetone yeast) with dextrose induces no acceleration in the normal rate of fermentation. In the presence of a suitable amount of phosphate, the effect of the aldehyde is greatly to diminish the time required for the attainment of the maximum, so that the volume of gas evolved in the period immediately following the addition of phosphate is greatly increased. At the same time, a considerably higher maximum is attained. On completion of the esterification of the phosphate, the rate again diminishes, both in the presence and absence of an aldehyde, and the total evolution is not greatly different in the two cases. Similar phenomena are produced by pyruvates.

The striking action of the aldehydes suggests that the cause of the delay in attainment of the maximum after the addition of the phosphate was lack of an acceptor for hydrogen. In order to test this idea, methylene-blue was substituted for aldehyde, with the result that it was found to produce a very similar effect.

The rôle of the hydrogen acceptors in the fermentation is discussed. It is probable that the hydrolysis of the hexosephosphate, both that originally present and that slowly formed in the fermenting mixture, results in the formation of lævulose, which in its turn yields a hydrogen acceptor, and thus assists the increase in the rate of fermentation. J. C. D.

A New Fixation Method and its Application in Alcoholic Fermentation. CARL NEUBERG and ELSA REINFURTH (*Biochem. Zeitsch.*, 1920, **106**, 281—291).—The authors have utilised Vorländer's observation that dimethyl*cyclo*hexanedione reacts with acetaldehyde, yielding ethylidenebisdimethyl*cyclo*hexanedione, for the fixation of acetaldehyde in the fermentation of sugar. In order to isolate the product, the yeast was centri-

fuged and extracted with hot alcohol. The alcoholic extract was concentrated and added to much water, when ethylidenebisdimethyl*cyclo*hexanedione was precipitated (m. p. 139—140°), and its nature confirmed by conversion into its anhydride, $C_{18}H_{24}O_3$, m. p. 173—175°, by heating with glacial acetic acid under reflux. Acetaldehyde can also be fixed in the above way when the sugar is fermented with maceration juice. Pyruvic acid is not fixed by dimethyl*cyclo*hexanedione. S. S. Z.

The Three Forms of the Fermentation of Sugar. Their Connexion and their Balance Sheet. CARL NEUBERG, JULIUS HIRSCH, and ELSA REINFURTH (*Biochem. Zeitsch.*, 1920, **105**, 307—336).—The relation of the three forms of fermentation (this vol., i, 798) was studied by estimating the quantity of fermented sugar and the products of fermentation at various periods of the processes. In all the three forms, the common product, acetaldehyde, is produced, which is reduced to alcohol in the first form of fermentation, is fixed by the sulphite in the second form of fermentation, and is converted into acetic acid and alcohol in the third "dismutation" form of fermentation. In all the three forms of fermentation, the fermented sugar was accounted for in the products of fermentation, which were produced in definite proportions. S. S. Z.

The Physical-chemical Conception of the Processes of Fermentation. WOLFGANG OSTWALD (*Biochem. Zeitsch.*, 1920, **105**, 305); C. NEUBERG (*ibid.*, 306).—Polemical. S. S. Z.

Influence of Fluctuating Barometric Pressure on the Course of Alcoholic Fermentation and of Biological Processes in General. AUGUST RIPPEL (*Centr. Bakt. Par.*, 1917, ii, **47**, 225—229).—In certain cases, it is found that the curve showing the periodic evolution of carbon dioxide from a fermenting solution exhibits a zig-zag course, high barometric pressure corresponding with low rate of fermentation, and vice versa. When the nutrient solution employed is such that a vigorous fermentation is rapidly established, the effect of the barometric pressure may not be evident in the early stages, but it becomes apparent when the action slackens. Such increased liberation or retention of gases, which are either merely present as such or represent the final products of a biological or chemical process, may have important effects on biological processes. T. H. P.

Comparative Studies on Respiration. XII. A Comparison of the Production of Carbon Dioxide by Penicillium and by a Solution of Dextrose and Hydrogen Peroxide. F. G. GUSTAFSON (*J. Gen. Physiol.*, 1920, **3**, 35—39).—A neutral solution of dextrose and hydrogen peroxide acts like *Penicillium chrysogenum* in producing an increased amount of carbon dioxide on the addition of acid, but not on the addition of alkali.

J. C. D.

Attackability of *cis*- and *trans*-Isomeric Unsaturated Acids by Moulds. P. E. VERKADE and N. L. SÖHNGEN (*Centr. Bakt. Par.*, 1920, ii, **50**, 81—87).—In solution containing excess of undissolved calcium carbonate, these acids exhibit the same behaviour towards *Aspergillus niger* as towards *Penicillium glaucum*; fumaric, cinnamic, *allo*cinnamic, aconitic, oleic, and erucic acids are assimilated readily, and glutaconic acid slightly, whereas maleic, citraconic, mesaconic, itaconic, phenylitaconic, *iso*crotonic, crotonic, ββ-dimethylacrylic, angelic, tiglic, undecenoic, elaidic, and brassidic acids are not attacked. Similar results are obtained when the free acids instead of their calcium salts are employed, excepting that with cinuamic acid no development of the two organisms takes place. It is evident that the attackability or non-attackability by mould fungi is inadmissible as a means of distinguishing between *cis-trans*-isomerides.

The behaviour of certain of these acids towards the moulds is explainable by their solubilities in water and in olive oil (compare Waterman, *ibid.*, 1915, II, **42**, 639), but that of other acids cannot be explained in this way. Assimilability or non-assimilability appears, indeed, to be dependent principally on the molecular configuration of the compound. T. H. P.

Favourable Influence of Selenium on some Moulds coming from the Cheese Industry. ANTONIN NĚMEC and VÁCLAV KÁŠ (*Compt. rend.*, 1920, **171**, 746—748).—With selenium in the form of sodium selenate, there is an increase in the weight of dry mycelium in the case of *Penicillium Roqueforti*, with increasing amounts of sodium selenate in the culture solution. With *P. candidum*, a toxic effect was noticed when the amount of sodium selenate increased beyond a certain limit. The ash content of the mycelium increased at first with the amount of selenium present, but reached a maximum and then diminished. W. G.

Specific Disinfection Processes. II. Action of Salts and Ions on Bacteria. PHILIPP EISENBERG (*Centr. Bakt. Par.*, 1918, , **82**, 69—208).—The author has carried out extensive series of experiments on the effects of inorganic salts in different concentrations on the development in peptone–meat extract–agar or bouillon of six gram-positive and six gram-negative bacterial species. The results are given in detail, and lead to the following, among other, conclusions. The toxicity of salts may be regarded as an additive function of their component ions, although purely molecular actions are not to be excluded. The commoner anions (cations) may be arranged in toxicity series, which vary appreciably for different cations (anions). The normal life functions of bacteria are connected with a state of swelling of the protoplasmic colloids definite for each species, and any deviation from this state in either direction may cause disturbance of these functions, or even death, of the bacteria; hence the toxicity of salts increases with their swelling properties, and also with their precipitating action on bacteria. The effects of salts on the gram-specificity of bacteria are discussed.

Various cases of species- or group-specificity are indicated. In evaluating antiseptics, it is necessary to employ a number of representative bacterial species. T. H. P.

Regularities in the Preservation of Wood. Poisoning Action of Inorganic Compounds (Salts) on Fungi. FRIEDRICH MOLL (*Centr. Bakt. Par.*, 1920, ii, **51**, 257—279).—The author has investigated a series of 130 different salts with respect to the effect they produce, in various concentrations, on a culture of *Penicillium glaucum* on a peptone–agar medium. The results obtained show that the poisonous action of salts is an additive property of the ions. In the order of diminishing activity, the poisonous ions are: mercury, silver, cadmium, cyanogen, copper, zinc, iron, cobalt, chromium, fluorine. Most acid ions and the ions of the alkali and alkaline earth metals, magnesium, and aluminium may be regarded as inactive in this respect. The poisonous action depends on the solubility in water of the salt and on its decomposition into ions in the aqueous solution. Every ion exhibits a specific poisonous action, and complex ions, such as the chromate and fluosilicic ions, must be regarded as independent individuals, their activity being equal to, or smaller, or greater than, the sum of their constituents. Addition of other salts to active substances may affect the time-course of the disinfection, but does not alter the final result. The activity of a given amount of a soluble salt or mixture of salts depends only on the quantity of active constituents present and on their specific effects. T. H. P.

Toxicity and Chemical Potential. W. LASH MILLER (*J. Physical Chem.*, 1920, **24**, 562—569).—The toxicity of a solution containing phenol and an indifferent salt depends primarily on the chemical potential of the phenol in the solution. Two solutions have the same toxicity when they are in equilibrium with the same solution of phenol in an immiscible solvent, such as toluene or petroleum. Complications may arise from the toxicity of the salts themselves, or in dilute solutions from the plasmolysis of the cell, independently of the toxicity of the solutions employed. One or two individual cases which do not fall under these heads are worthy of further study. The observation of Paul and Krönig that solutions of mercuric chloride in aqueous alcohol show a maximum of toxicity when the ratio of alcohol to water in the solution is 1 to 3 affords another illustration of the principle, since Laird has shown that the solubility of mercuric chloride in aqueous alcohol passes through a minimum at the same ratio. J. R. P.

The Toxicity towards Anthrax and Staphylococcus of Solutions containing Phenol and Sodium Chloride. J. S. LEMON (*J. Physical Chem.*, 1920, **24**, 570—584).—Experiments with anthrax spores showed that the increased toxicity of phenol observed when sodium chloride is added to its solution is in accordance with the assumption that two solutions of phenol, with

or without salt, are equally toxic if their compositions are such that both would be in equilibrium with the same solutions of phenol in toluene. Experiments with *Staphylococcus*, in which lower concentrations of phenol were used, showed that whilst the assumption is in fair accord with the behaviour of 0·80% phenol, in the case of 0·60% phenol, the chemically equivalent solution containing salts is much less toxic; 0·70% phenol occupies an intermediate position.

J. R. P.

Disinfecting Values of the Three Isomeric Cresols. FRITZ DITTHORN (*Centr. Bakt. Par.*, 1919, i, **82**, 483—491).—Experiments made with suspensions of *Bacillus coli*, *B. pyocyaneus*, and *Staphylococcus* in sodium chloride solution and in bouillon show that *m*-cresol outstrips its two isomerides in germicidal power, which is not very marked in the salt and bouillon suspensions, but is considerable in liquids containing proteins (ascites). Of the two other isomerides, the ortho-compound possibly has a slightly greater action than the para-compound. In practice, 2—2·5% solutions of a mixture of the isomerides are used, and the differences observed are then of little importance, the germicidal powers of 0·75—1·0% solutions of the three compounds being almost identical.

T. H. P.

Organic Carbon Nutrition of Plants. Parallels between Fungi and Green Plants. TH. BOKORNY (*Centr. Bakt. Par.*, 1917, II, **47**, 191—224, 301—375).—The author gives a summary of the observations made by various investigators with reference to the use by fungi and green plants of compounds of the following classes: alcohols, phenols, aldehydes, ketones, ketonic esters, organic acids, carbohydrates, amino-compounds, and cyanogen derivatives.

T. H. P.

Reduction of Nitric Acid in Green Cells. OTTO WARBURG (*Naturwiss.*, 1920, **8**, 594—596; from *Chem. Zentr.*, 1920, iii, 487).—Attempts to accelerate catalytically the reduction of nitric acid by *Chlorella vulgaris*, Beyerinck, by the use of concentrated nitrate solutions were unsuccessful, but signs of acceleration were noted in dilute solutions of free nitric acid. In an acidic nitrate mixture ($N/100$-HNO_3, $N/10$-nitrate), the reduction of nitric acid amounts to 50% in the dark and to 150% in the presence of light of the total metabolism. In the former case, reaction occurs according to the equation $HNO_3 + H_2O + 2C = NH_3 + 2CO_2 + 162{,}000$ cal. Under the action of light, the process is complicated by the assimilation of carbon dioxide, which, however, can be excluded by use of narcotics.

H. W.

Possible Formation of Hexamethylenetetramine in Assimilating Plants, and a Microchemical Reaction for Ammonium Salts. C. VAN ZIJP (*Pharm. Weekblad*, 1920, **57**, 1345—1348).—The combination of formaldehyde with ammonium salts in neutral, or even weakly acid, solution is found to give salts

of hexamethylenetetramine, in the same way as the base itself is formed by combination of the aldehyde with free ammonia; hence it is likely, since both formaldehyde and ammonium salts are present in growing plants, that salts of hexamethylenetetramine are also formed in the plant. The iodine–potassium iodide reagent employed by the author in the microchemical identification of hexamethylenetetramine is found to be suitable also for its salts. The test will detect 0·3 mg. of hexamethylenetetramine, and half this quantity of ammonium salt. It is therefore an extremely sensitive test for ammonium salts, and has the advantage that potassium salts do not interfere. The limit of sensitiveness is beyond the degree of solubility even of magnesium ammonium phosphate, since if a drop of formalin is added to a drop of water in which this substance is suspended, the residue, after drying gives the characteristic brown crystals with the iodine–potassium iodide solution. It is suggested that the ammonia is withdrawn from the phosphate molecule by the aldehyde, leaving the phosphate, $MgHPO_4$. S. I. L.

The Factors which Interfere with the Use of Yeast as a Test Organism for the Antineuritic Substance. GERALDO DE PAULA SOUZA and E. V. MCCOLLUM (*J. Biol. Chem.*, 1920, **44** 113—129).—The observations made by the authors lead them to conclude that the use of yeast as a test organism for determining the presence or absence of the vitamin-*B* is complicated by so many disturbing factors as to make it of little, if any, value.

J. C. D.

Silver-reducing Cell-substances in the Leaves of Non-conifers. FRIEDRICH CZAPEK (*Ber. Deut. bot. Ges.*, 1920, **38** 246—252).—Molisch (*Sitzungsber. Akad. Wiss. Wien, Math. nat Kl.*, 1918, I, **127**, 449) has shown that a 0·1—1% silver nitrat solution produces in the epidermis, especially of leaves of flowerin plants, a deep black coloration of the chloroplasts; this reactio he ascribes to the presence of an extremely labile substance, whic loses its reducing power even when the chlorophyll plasma die If the views expressed by Molisch were accurate, this reactio would represent a new "life reaction."

According to the author, however, it appears demonstrable tha the cause of the silver reduction of the chloroplasts is to be sough in the presence of various depsides, which are probably not con nected with the process of assimilation of carbon dioxide.

T. H. P.

The Preparation of Phosphatides from Coloured Plar Organ R. FRITSCH (*Zeitsch. physiol. Chem.*, 1919, **10** 165—1 .—Various plants containing chlorophyll and other plar pigmen have been examined for their phosphatide content. Onl a smal art of the total phosphorus could be traced to th ... of the plants. In the leaves of the maple, th

phosphatide phosphorus amounted to 4·78%; in the leaves of the ash to 3·46% of the total phosphorus. No calcium inosinate was found in the green assimilating organs. In order to obtain phosphatides with the theoretical content of phosphorus, large quantities of tissue must be employed. In grass stored in silos, the phosphatides are almost entirely decomposed. S. S. Z.

Oxidising Enzymes. II. The Nature of the Enzymes Associated with Certain Direct Oxidising Systems in Plants. Muriel Wheldale Onslow (*Biochem. J.*, 1920, **14**, 535—540. Compare A., 1919, i, 361).—Solutions of certain compounds, such as catechol, which contain the *o*-dihydroxy-structure, tend to undergo autoxidation when exposed to air with the formation of peroxides. On addition of a solution of peroxydase to these peroxides, an oxydase system is produced which will give the blue colour with guaiacum. The autoxidation of the substances with the *o*-dihydroxy-grouping is accelerated by enzyme extracts of plants which turn brown on injury, and of which the juices turn guaiacum blue without the addition of hydrogen peroxide. Such plants have been found to contain a compound giving the "catechol" reaction, and it is suggested that they also contain an enzyme "oxygenase," which accelerates the production of a peroxide. This enzyme can be separated from peroxydase by fractional precipitation with alcohol, although the converse has not been accomplished.

In the cases which have been investigated, the oxydase system appears to consist of three components: a "catechol" compound from which a peroxide can be formed, oxygenase which catalyses this process, and a peroxydase which decomposes the peroxide with formation of "active" oxygen. J. C. D.

Oxidising Enzymes. III. The Oxidising Enzymes of Some Common Fruits. Muriel Wheldale Onslow (*Biochem. J.*, 1920, **14**, 541—547).—The apple fruit contains the complete oxydase system (see preceding abstract). A large amount of the aromatic compounds of the fruit appears to be present in the form of a catechol tannin, which cannot be activated by the enzyme in vitro. The quince, pear, plum, greengage, and damson also contain oxydase. In the case of the banana, both skin and flesh appear to contain peroxydase and oxygenase, but the "catechol" substance is practically absent from the flesh. The fruits of the orange, lemon, and lime contain peroxydase in both the rind and pulp, but no oxygenase or "catechol" substance was found present. The raspberry contains peroxydase, but no oxygenase or catechol substance. J. C. D.

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